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ON THE BEHAVIOR OF SODIUM AND SODIUM ALCOHOLATES TOWARDS VARIOUS ESTERS OF ACETIC ACID.

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An exhaustive study, covering a period of over 10 years, by Nef[1] of the primary and secondary alcohols, their salts and ethers, has proved that all these compounds are partially dissociated into alkylidene and water or metallic hydroxide, respectively,

$$RR'CHOM \rightleftarrows RR'C\!<\!\!\!

$$RR'CHX \rightleftharpoons RR'C< + HX$$

[X = Cl, Br, I, ONO_2, $OCOCH_3$, $\frac{1}{2}SO_4$, etc.].

The only difference is that the percentage of dissociation which exists at ordinary temperatures in the substances named varies (1) with the nature of the alkyl radical, and (2) with the nature of X or of OM.

It follows from this that all the known reactions of the primary and secondary alkyl halides, etc., with ammonia, benzene, etc., and with salts of various substances, such as acetic acid, acetoacetic ester, etc., can no longer be interpreted from the standpoint of metalepsis, but depend upon the fact that alkylidene dissociation exists to a greater or less degree in the various reagents used; the speed of the reaction in a given instance must, obviously, be directly proportional to the amount of existing dissociation. Thus, when sodium acetoacetic ester reacts with ethyl iodide, nitrate, or sulphate to give α-ethyl acetoacetic ester and sodium iodide, nitrate or monoalkyl sulphate, respectively, the reaction proceeds in successive stages, as follows: The HX

[X = I, ONO_2 or OSO_2OR]

present as a product of dissociation acts on sodium acetoacetic ester,

$$CH_3C(ONa) : CHCOOR,$$

forming NaX and setting free acetoacetic ester, which is then absorbed at once by the alkylidene according to

$$CH_3CH< + H—C(COOR) : C(OH)CH_3 \rightarrow CH_3CH_2—C(COOR) : C(OH)CH_3.$$

This reaction, therefore, belongs to the category of alkylidene condensations;[1] and the enormous number of analogous carbonyl and ethylene condensations observed in the last 18 years, especially by Michael, Auwers, Knovenagel and Vorländer in the case of acetoacetic ester and allied compounds with aldehydes, ketones, and olefines (in the presence of sodium alcoholates, or traces of primary and secondary

[1] Cf. Nef: Ann. Chem. (Liebig), 298, 202-231.

amines) must be regarded as important experimental evidence tending to establish the correctness of this interpretation of the reaction.[1] It is interesting to notice that the ethylidene does not absorb acetoacetic ester to give a trace of β-ethoxyisocrotonic ester,

$$\begin{matrix} CH_3COCH_2CH_3; \\ \| \\ HC—COOR \end{matrix}$$

furthermore, it is *certain* that this compound is not an intermediate product in the reaction under discussion.

It is important, therefore, to realize that in most of the reactions in which acetoacetic ester or its salt is absorbed by unsaturated compounds, as alkylidenes, olefins, ketones, aldehydes, nitriles, etc., it is *not* the ionic hydrogen atom,

$$\begin{matrix} CH_3CO—H, \\ \| \\ HCCOOR \end{matrix}$$

but the *non-ionic* hydrogen atom bound to the α-carbon atom,

[1] The interpretation of Michael that the ethyl iodide adds itself directly to sodium acetoacetic ester, giving first an addition product, $CH_3C(ONa)ICH(COOR)C_2H_5$, an interpretation which I also formerly adopted (Ann. Chem. (Liebig), **266**, 59–62), is no longer tenable and was given up by me 9 years ago (Ann. Chem. (Liebig), **298**, 263–269). My work since has shown that the long-known reactions of dialkyl sulphides and tertiary amines with alkyl halides which result in the formation of trialkyl sulphinium halides, $R_3 \vdots SX$, and quaternary ammonium halides, $R_4 \vdots NX$, proceed in *three* successive stages (Ann. Chem. (Liebig), **309**, 162–3; **318**, 1–57). There is, consequently, at the present time not a single instance known where an alkyl halide is added directly to an unsaturated compound or atom in the manner assumed by Michael.

Furthermore, the stable addition products recently described by him (Ber. d. chem. Ges., **38**, 3217), with chloracetic ester, sodium acetoacetic ester and malonic ester do not exist, but have been proved by Paal (Ber. d. chem. Ges., **39**, 1436) to consist simply of a mixture of the alkylated derivative and colloidal sodium chloride. I might mention, that I observed, in 1890, in connection with my experiments with sodium acetoacetic ester and acyl chlorides, that almost clear solutions were at first obtained on mixing the reagents in the presence of ether; this observation, as well as other data, led me to the conclusion, at that time, that addition products of the character assumed by Michael must have been formed. We are obviously, however, dealing here simply with a mixture of sodium chloride in colloidal solution and the acylated derivatives of acetoacetic ester.

The addition products recently mentioned by Bushong and by Willcox (THIS JOURNAL, **30**, 216; **32**, 448; cf. also Ephraim: Ber. d. chem. Ges., **38**, 778; **39**, 1905), and obtained by them from chlorsulphone ethyl ester and sodium alcoholates, in absolute ethereal solution, are obviously also mixtures of ethyl alkyl sulphate and sodium chloride in colloidal solution. J. U. NEF.

$$\begin{matrix} CH_3COH \\ \| \\ HCCOOR \end{matrix},$$

which is torn from the atom to which it is bound. The obvious consequence of this is that the condensation or addition products obtained contain the residue introduced bound to the α-carbon atom of acetoacetic ester.[1] When sodium α-ethyl acetoacetic ester,

$$\begin{matrix} CH_3CONa \\ \| \\ C_2H_5CCOOR \end{matrix},$$

is converted by ethyl iodide, nitrate, or sulphate into α-diethylacetoacetic ester the ethylidene absorbs similarly the *non-ionic* keto-α-ethylacetoacetic ester molecules present

$$CH_3CH\!\!<\!\!\!\!\diagup \; + \; H-\overset{\displaystyle COCH_3}{\overset{|}{C}}(C_2H_5)COOR$$

(cf. foot-note), to give the product,

$$CH_3CH_2C(C_2H_5)(COCH_3)COOR,$$

actually obtained.

It is usually supposed that only alkyl halides can act as alkylating agents, but in view of the new theory of Nef, presented in part above, it is clear that not only these substances but also any compound giving alkylidene by dissociation, can act as an alkylating agent.[2] This explains why the alkyl sulphates and nitrates are so valuable and have so long been used commercially as alkylating agents. It also follows logically from Nef's work that the "cracking" of petroleum

[1] One can also assume that the anion of acetoacetic ester, $\begin{matrix} CH_3C-O- \\ \| \\ HCCOOR \end{matrix}$, rearranges with great speed into $\begin{matrix} CH_3C:O \\ | \\ -HCCOOR \end{matrix}$, and is then absorbed by one affinity unit of an unsaturated compound; this is perfectly analogous to the rearrangement of the anion of nitrous or prussic acid, cf. Ann. Chem. (Liebig), **309**, 150. At the present time, I consider this as the most justifiable interpretation of the reaction and the same idea may also be applied to the aldol condensation. J. U. NEF.

[2] Ann. Chem. (Liebig), **309**, 180.

which results in the splitting as well as in the building up of the carbon chains in the paraffins, is similarly due to alkylidene dissociation, etc. We know from the experiments of Dennstedt[1] that ammonia, pyrrole, primary and secondary amines, phenols, etc., can be alkylated by alcohols in the presence of zinc dust, at 250°. These reactions, as Nef has shown, depend upon an intermediate formation of zinc alcoholate, which must at once dissociate completely, under the existing temperature conditions, into zinc hydroxide and alkylidene, and the latter substance must then absorb the ammonia, phenol, etc., to give the alkylated derivatives which were obtained.

Nef has shown that the metallic alcoholates, RR′CHOM, where M = Ca, Ba, Zn, Na, K, etc., have very low decomposition points, 200°–250°; consequently, much dissociation, according to $RR_1C< + HOM$, exists at ordinary temperatures. This explains why the salts of primary and secondary alcohols are spontaneously combustible and also why these substances act as alkylating agents. Thus it has been found that aniline can be alkylated by means of sodium alcoholates at 200°–250°; Nef was also able to prove[2] that when the ionic hydrogen atom is removed or replaced it is possible to alkylate, by means of sodium alcoholates, with especial ease, the α-hydrogen atoms present in acetic acid and its mono- and dialkylated substitution products,

$$CH_3COOM, \qquad RCH_2COOM, \qquad RRCHCOOM.$$

By similar treatment the non-ionic hydrogen atom in formic acid derivatives, HCOOM, can be replaced by alkyl (methyl, ethyl, diphenyl methyl) to a slight extent, giving thus the monoalkylated formic acids, RCOOM. Nef interpreted his experiments with sodium alcoholates and ethyl acetanilide at 150° on the basis of a direct union of the alkylidene with ethyl acetanilide,

$$RCH< + H—CH_2CON(C_2H_5)C_6H_5 \rightarrow RCH_2CH_2CON(C_2H_5)C_6H_5.$$

[1] Ber. d. chem. Ges., **23**, 2563–70.
[2] Ann. Chem. (Liebig), **318**, 143–182.

It was, however, obvious from the experiments of Geuther and Claisen, with acetic ester and sodium ethylate, that these reactions might be due to an intermediate formation of acetoacetic ester. This compound would then, naturally, under the conditions of the experiment, 150°, unite at once with the alkylidene present to give the mono- and di-α-alkylated acetoacetic esters; these must then obviously undergo an "acid splitting" in the presence of the sodium hydroxide and thus give rise to the mono- and dialkylated acetic acids obtained by Nef and Geuther in their syntheses. I, therefore, began experiments at once in this direction at the suggestion and under the guidance of Dr. Nef and was soon able to prove an intermediate formation of acetoacetic ester from mixtures of ethyl acetanilide and sodium alcoholates at 100°—so that there is now no doubt that many of these syntheses take place through an intermediate formation of an acetoacetic ester. There are, however, many instances where the alkylation of the acetyl radical takes place directly and still other cases where it is impossible, from the existing evidence, to decide between these two interpretations—which necessarily however, lead to the same end result. The alkylation of a formyl group, as well as of the tertiary hydrogen atom in isobutyl,

$$\begin{array}{l} H-C(CH_3)_2 \\ | \\ OCOM \end{array},$$

by sodium alcoholates must, of necessity, take place directly, since the formation of an acetoacetic acid derivative is impossible. These investigations led me, further, to a careful study of the action of sodium and of sodium alcoholates on various esters of acetic acid and a very brief statement of some of my results has appeared in the papers of Beatty and of Bacon.[1] I have also studied the behavior of sodium benzylate towards heat and towards dry oxygen and have proved that it acts as an alkylating agent.

[1] THIS JOURNAL, 30, 225, foot-note; 33, 79-80.

EXPERIMENTAL PART.

Ethyl Acetate and Sodium Ethylate.—It may now be considered as definitely established through Claisen's experiments[1] that sodium ethylate is the active condensing agent when acetic ether is converted into sodium acetoacetic ester by means of sodium. The isolation by Claisen of the addition product, $C_6H_5C(ONa)(OC_2H_5)_2$, proves that here also an analogous ortho derivative must first be formed, which then, according to his former interpretation, splits off 2 molecules of alcohol by metalepsis with a second molecule of acetic ester,

$$CH_3C(ONa)(OC_2H_5)_2 + H_2CHCOOR \rightarrow CH_3C(ONa) : CHCOOR + 2C_2H_5OH,$$

giving thus sodium acetoacetic ester. Nef has shown[2] that this reaction should be classed among the olefin condensations, *i. e.*, that the ortho addition product first formed loses 1 molecule of alcohol,

$$CH_3C(ONa)(OC_2H_5)_2 \rightarrow CH_3C\begin{matrix}\diagup ONa \\ \diagdown OC_2H_5\end{matrix} + C_2H_5OH,$$

giving thus sodium *iso*acetic ester, which then immediately absorbs a second molecule of acetic ester,

$$CH_2{=}C\begin{matrix}\diagup ONa \\ \diagdown OC_2H_5\end{matrix} + H{-}CH_2COOR \rightarrow CH_3C(ONa)(OC_2H_5)CH_2COOR,$$

giving as the end product, by further loss of 1 molecule of alcohol, sodium acetoacetic ester. The reaction is, furthermore, as Nef has first pointed out, reversible, and this explains most simply the so-called "acid splitting" of acetoacetic ester, as well as of its mono- and di-α-alkylated substitution products.

E. von Meyer and Friessner[3] have recently studied the action of sodium ethylate on ethyl acetate at various temperatures and

[1] Ber. d. chem. Ges., **20**, 636; cf. Ann. Chem. (Liebig), **297**, 92-8.
[2] Ann. Chem. (Liebig), **298**, 320.
[3] J. prakt. Chem. [2], **65**, 528.

found that the maximum yield of sodium acetoacetic ester is only 36.1 per cent of that demanded by the theory after 2 hours' heating at 100°. They found, further, that temperatures above 140° depress the yield most strikingly and that only small yields are obtained at ordinary temperatures. On account of the last named observation, and because metallic sodium gives with acetic ester a relatively larger yield of sodium acetoacetic ester at ordinary temperatures, Michael[1] still disputes the conclusion of Claisen that sodium ethylate is the active condensing agent in the reaction under discussion. He assumes that acetic ester and sodium first give hydrogen and sodium acetic ester according to

$$H—CH_2COOR + Na \rightarrow NaCH_2COOR + H,$$

and that sodium acetic ester is thereupon absorbed by acetic ester,

$$CH_3C(=O)OC_2H_5 + Na—CH_2COOR \rightarrow CH_3C(ONa)(OC_2H_5)CH_2COOR;$$

the addition product thus formed must then give, by loss of alcohol, sodium acetoacetic ester, as shown above. I have found, contrary to E. von Meyer and Friessner's observations, that mixtures of 36 grams of ethyl acetate (2 mols.) and 10 grams of sodium ethylate, on standing for 7 and for 25 days, respectively, give 5.1 grams and 6.9 grams of pure acetoacetic ester, boiling at 175°–177° (uncor.). The amount in the first case was, therefore, 26.7 per cent and in the second 36.1 per cent of that demanded by the theory. Furthermore, it is well known that dilution with alcohol affects the yield most strikingly. These results show that the reaction between sodium ethylate and ethyl acetate takes place with measurable speed at 20° and reaches the equilibrium point only after about 25 days, whereas, at 100°, according to von Meyer and Friessner's observations, this point is reached after 2 hours. The conclusion, finally, of Michael that metallic sodium reacts *directly* with ethyl acetate to give hydrogen

[1] Ber. d. chem. Ges., 33, 3731 and 38, 1922; cf. Claisen: Ber. d. chem. Ges., 38, 709.

and sodium acetic ester is untenable, (i) because experiments (described below) with sodium and with acetic ester dissolved in 5 parts of absolute ether prove that *no trace* of hydrogen or of sodium acetoacetic ester is formed; (ii) because ethyl butyrate and ethyl caproate give, with metallic sodium, no trace of hydrogen but, almost quantitatively, ketol derivatives[1] according to

$$2CH_3CH_2CH_2-C:O(OC_2H_5) + 4Na \rightarrow$$

$$CH_3CH_2CH_2C(OC_2H_5)ONa \quad C_3H_7C:O$$
$$| \quad + 2Na \rightarrow \quad | \quad +$$
$$CH_3CH_2CH_2C(OC_2H_5)ONa \quad C_3H_7C:O$$

$$2Na + 2NaOC_2H_5 \rightarrow \begin{matrix} C_3H_7C\ ONa \\ \| \\ C_3H_7C\ ONa \end{matrix} + 2C_2H_5ONa;$$

and (iii) because propionyl, butyryl and isovaleryl chlorides give, on treatment with metallic sodium, no trace of hydrogen or of an acetoacetic ester-like derivative, but acylated dioxydialkyl ethylenes, which are also ketol derivatives,

$$\begin{matrix} RCOCOR \\ \| \\ RCOCOR \end{matrix},$$

and are formed[2] in a manner perfectly analogous to the dialkylated dinatroxyethylenes obtained by Bouveault and Locquin (under ii).

The fact that the monomolecular quantity of ethyl acetate, when diluted with absolute ether, gives, with the diatomic amount of sodium, large quantities of sodium ethylate besides dimethylketol, $CH_3CH(OH)COCH_3$ (see below), but no trace of hydrogen or of sodium acetoacetic ester, is of the greatest importance. It proves, taken in connection with Bouveault and Locquin's results,[3] (i) that an interaction between sodium and acetic ester, according to Michael,

$$H-CH_2COOR + Na \rightarrow NaCH_2COOR + H,$$

[1] Bouveault and Locquin: Comptes rendus, **140**, 1593. Hantzsch: Ann. Chem. (Liebig), **249**, 54; **246**, 129. Nef: Ann. Chem. (Liebig), **308**, 283–292. Acree: This Journal, **29**, 588. Bacon: This Journal, **33**, 78.

[2] Klinger: Ber. d. chem. Ges., **16**, 995; **19**, 1863; **24**, 1264; **31**, 1217. Cf. Nef: Ann. Chem. (Liebig), **308**, 283–289.

[3] *Loc. cit.*

cannot possibly take place; (ii) that a reaction between these reagents takes place according to

$$2CH_3COOR + 4Na \rightarrow \begin{matrix} CH_3C(OR)ONa \\ | \\ CH_3C(OR)ONa \end{matrix} +$$

$$2Na \rightarrow \begin{matrix} CH_3CONa \\ \| \\ CH_3CONa \end{matrix} + 2NaOR$$

and that this is the *only* reaction taking place when an indifferent solvent, like ether, is present to dilute the acetic ether and precipitate the sodium ethylate as soon as it is formed, thus preventing the possibility of the unchanged acetic ester and the sodium ethylate from acting upon each other to give alcohol (2 mols.) and sodium acetoacetic ester according to Geuther and Claisen.

It is, furthermore, exceedingly probable that when undiluted acetic ester is treated directly with metallic sodium—which I understand is the method used in the manufacture of acetoacetic ester—2 entirely independent reactions take place simultaneously, *viz.*, (i) in which the sodium reacts directly with the acetic ester according to

$$2CH_3COOC_2H_5 + 4Na \rightarrow \begin{matrix} CH_3CONa \\ \| \\ CH_3CONa \end{matrix} + 2NaOC_2H_5$$

and another reaction in which the sodium ethylate formed in (i) or by the action of sodium on the free alcohol present, reacts at once with the excess of acetic ester present, according to Geuther and Claisen,

$$2CH_3COOC_2H_5 + NaOC_2H_5 \rightarrow$$
$$CH_3C(ONa) : CHCOOC_2H_5 + 2C_2H_5OH,$$

giving free alcohol and sodium acetoacetic ester. The alcohol thus set free then reacts at once with the sodium present to give hydrogen and sodium ethylate so that the *main reaction* is obviously the formation of sodium acetoacetic ester under these conditions. Both Claisen and Friessner emphasize that the amount of hydrogen set free in the reaction between ethyl acetate and sodium is noticeably less than that

demanded by theory, and Claisen, therefore, concludes that some of the atomic hydrogen set free is used up in reducing ethyl acetate. The discrepancy is now self-evident since sodium and ethyl acetate can react upon each other according to reaction (i) without any evolution of hydrogen and with formation of much sodium ethylate. In view of all these considerations it should be more advantageous to manufacture acetoacetic ester from ethyl acetate and alcohol-free sodium ethylate, for under these conditions a reaction can take place only in one direction but not completely, because the reaction is reversible and reaches the equilibrium point when about 36.5 per cent of sodium acetoacetic ester is formed. Furthermore, it is my conviction that the greater yield and ease of action when sodium, instead of sodium ethylate, is used with ethyl acetate—points which are emphasized both by Claisen and by Michael—will, by further investigation, be found capable of a very simple explanation. It follows, for instance, from Nef's work[1] that sodium acetic ester must go over spontaneously, by intramolecular addition, into sodium isoacetic ester; an addition of the hypothetical sodium acetic ester to another molecule of ethyl acetate, as assumed by Michael, is, therefore, in the highest degree improbable.[2]

Ethyl Acetanilide and Sodium Ethylate.—Forty-six and one-half grams of ethyl acetanilide (2 mols), b. p. 148° (31 mm.), and 9.7 grams of sodium ethylate were intimately mixed by shaking in a sealed tube and then heated at 100° for 30 hours, 8 hours daily. The mixture was treated with an excess of dilute sulphuric acid and the oil which separated was extracted with ether, then dried with calcium chloride. On fractionation, 5.7 grams of acetoacetic ester, besides 8 grams of unchanged ethyl acetanilide, boiling at 148°–152° (35 mm.) and 3.4 grams oil boiling above 170° (35 mm.), were obtained. The acetoacetic ester which boiled at 175°–177° (uncor.) was identified by conversion into β-phenylhy-

[1] Ann. Chem. (Liebig), **308**, 284.

[2] In his latest papers Michael assumes that sodium reacts on ethyl acetate to give directly sodium isoacetic ether and hydrogen; such an interpretation is now also obviously untenable. I concur, however, with Michael's conclusion that the ethyl acetate absorbs the sodium isoacetic ester (see foot-note above). J. U. NEF.

drazidoisocrotonic ester and into 1-phenyl-3-methylpyrazolone (6.4 grams, m. p. 127°). The sulphuric acid solution gave, upon making alkaline with sodium hydroxide, 24.9 grams of ethyl aniline boiling at 94°–95° (20 mm.).

These results prove that 37 per cent of the theoretical amount of acetoacetic ester was formed according to

$$2C_6H_5(C_2H_5)NCOCH_3 + NaOC_2H_5 \rightarrow CH_3C(ONa) : CHCOOR + 2C_6H_5NHC_2H_5;$$

the addition product,

$$CH_3C(ONa)(OC_2H_5)N(C_6H_5)C_2H_5,$$

is, obviously, an intermediate product in this case.

The formation of ethyl,- isobutyl-, and isoamylacetic acids from equal molecules of ethyl acetanilide and the corresponding sodium alcoholates, at 150°–240°, as observed by Nef,[1] must, therefore, be due to an intermediate formation of acetoacetic ester with subsequent alkylation and "acid splitting," as explained in the introduction. It is possible to interpret in a similar manner the reaction of sodium ethylate and sodium acetate, at 200°–210°, alone and in the presence of carbon monoxide, whereby, according to the observations of Geuther and Beatty,[2] mono- and diethylacetic acid are formed. Beatty observed, in connection with these experiments, that on mixing cold alcoholic solutions of potassium acetate and sodium ethylate a very voluminous, crystalline precipitate formed, which was assumed by him to be an ortho addition product, $CH_3C(OK)(ONa)OC_2H_5$.

On repeating the experiment with 1 gram of sodium and 5 grams of potassium acetate and separating the salt, 1.9 grams of fine, silky, white needles were obtained. These were found, however, to consist of pure sodium acetate, as shown by the following analyses:

0.2918 gram substance gave 0.2504 gram Na_2SO_4.

0.3840 gram substance gave 0.2722 gram NaCl.

0.3725 gram substance gave 0.3980 gram CO_2 and 0.1302 gram H_2O.

[1] *Loc. cit.*

[2] THIS JOURNAL, 30, 242.

0.3252 gram substance gave 0.3444 gram CO_2 and 0.1167 gram H_2O.

	Calculated for $C_2H_3O_2Na$.	Found. I.	Found. II.
Na	28.08	27.82	27.92
C	29.23	29.13	28.87
H	3.70	3.91	4.01

Special experiments with sodium ethylate and sodium acetate, as well as with the corresponding potassium salts, have shown decisively that no union to form an ortho addition product took place at the ordinary temperature. The fact that acetic anhydride and sodium acetate react more energetically as an acylating agent than either reagent separately—as well as the observation of Perkin, Sr., that these reagents, when heated to 180°, give carbon dioxide and acetone, also points to an intermediate formation of an acetoacetic acid derivative and, therefore, also of an ortho addition product, $CH_3C(ONa)(OCOCH_3)_2$. The conversion of calcium acetate at higher temperatures into calcium carbonate can, obviously, also be understood on an analogous basis. Similarly, the constitution of the abnormal acid salts of potassium acetate and of potassium oxalate may be interpreted from this standpoint, *e. g.*, the very stable salt, $KOCOCH_3.HOOCCH_3$, being $CH_3C(OH)(OCOCH_3)OK$, etc.

The Dissociation of Sodium Benzylate.—The sodium benzylate used in all my experiments was prepared from fine sodium wire suspended in 25 parts of absolute ether, by addition of the calculated amount of benzyl alcohol and heating until all the metal disappeared. The ether was then removed by distillation in a stream of dry hydrogen and the salt remaining was, finally, heated in a bath raised to 180°.

Fifty grams of sodium benzylate were heated in a distilling flask connected, successively, with a condenser, a receiver, and an azotometer. As soon as the temperature of the surrounding bath reached 200° the salt began to melt and at 240° the molten mass began to decompose rapidly, with formation of gaseous and volatile liquid products. The temperature of the bath rose, finally, after 9 hours' heating, to 305°. By

this time the gas evolution had practically ceased and the material in the distilling flask had entirely solidified and was colored yellow.

Four and five-tenths grams of mobile oil had collected in the receiver and the total amount of gas obtained was 3255 cc. Duplicate analyses of the later portion of the gas by Hempel's methods proved that it consisted mainly of hydrogen: Hydrocarbons, 1.4 per cent; carbon monoxide, 0.4 per cent; hydrogen, 91.5 per cent; oxygen, 1 per cent; and nitrogen, 5.7 per cent. The hydrocarbons were determined by absorption with alcohol; the hydrogen was determined in one case by absorption with palladium and in the other by explosion with air.

The 4.5 grams of oil in the receiver were found, by fractionation, to consist mainly of toluene, 3.3 grams boiling at 85°–115° and containing, therefore, small amounts of benzene; in addition, 1.2 grams of benzyl alcohol, boiling at 200°–201°, were obtained.

On adding 400 cc. of water to the residue left in the distilling flask, extracting with ether, etc., much neutral oil was obtained. This, upon fractionation under reduced pressure, gave 4.2 grams of benzyl alcohol, 1.5 grams of dibenzyl and 3 grams of non-volatile tar. The dibenzyl was purified by crystallization from ether and obtained in plates, melting unchanged at 51° when mixed with a known preparation of the substance.

Steam was now passed through the aqueous alkaline solution and, on cooling, an insoluble substance crystallized out, which, on recrystallization from alcohol, melted at 134° and weighed 1.4 grams. It was identified as benzoin by conversion into the β-phenylhydrazone of Smith and Ransom, m. p. 106°.[1]

On acidifying the alkaline solution with sulphuric acid no trace of carbon dioxide was obtained; the aqueous solution, on extracting with ether, etc., gave a total of 21.5 grams of crystalline residue. Only a portion of this dissolved in sodium carbonate, giving, finally, 9.2 grams of benzoic acid, m. p.

[1] THIS JOURNAL, 16, 112.

121°; the remainder consisted of a yellowish tar, neutral to sodium carbonate but soluble in caustic alkalies.

The formation of most of these products can readily be understood on the basis of Nef's work.[1] The main reaction is evidently conversion into benzoic acid and hydrogen, according to Dumas and Stas, a reaction which takes place quantitatively when benzyl alcohol is heated to 250° in the presence of an excess of potassium hydroxide or of soda lime.

A portion of the phenylmethylene, formed by dissociation of the sodium benzylate, is reduced to toluene and to phenylmethyl, which polymerizes at once to dibenzyl. Part of the benzoic aldehyde, which is an intermediate product in the Dumas-Stas reaction, condenses to benzoin and another portion is split, to a very limited extent, into benzene and carbon monoxide. The regeneration of large amounts of benzyl alcohol indicates incomplete action or that water must have been formed in the reaction and, finally, the formation of large amounts of acid and neutral tars is due to the known tendency of phenylmethylene and of hydroxyphenylmethylene to form condensation products.

On the Oxidation of Sodium Benzylate in Dry Air.—According to Nef's interpretation of combustion phenomena,[1] the following reactions between the dissociated sodium benzylate molecules and the active oxygen molecules in the air must take place at considerable speed on passing dry air and oxygen over this salt at ordinary temperatures:

$$\text{(I)}\quad \rangle C_6H_5CH\langle + 2Na - OH + \underset{|}{O} - \underset{|}{O} \rightarrow$$

$$C_6H_5CH(OH)_2 + NaO.ONa \rightarrow C_6H_5CHO + H_2O + Na_2O_2;$$

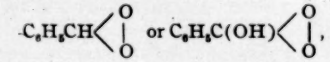
$$\text{(II)}\quad \begin{matrix} C_6H_5 \\ NaO \end{matrix}\rangle C\langle + 2Na - OH + \underset{|}{O} - \underset{|}{O} \rightarrow$$

$$C_6H_5C(OH)_2ONa + NaO.ONa \rightarrow C_6H_5CO(ONa) + H_2O + Na_2O_2.$$

This was found to be the case. The water liberated, ac-

[1] Ann. Chem. (Liebig), 318, 173.
[2] *Ibid.*, 298, 294-301, 322-332; 318, 177-182.

cording to I. and II., sets free much benzyl alcohol which is, therefore, found unchanged at the end of the experiment. The sodium peroxide is, however, in great part used up in oxidizing the unchanged phenylmethylene and hydroxyphenylmethylene particles, so that only 1.4 per cent of the theoretical amount of Na_2O_2 was found at the end of the experiment. No trace of a peroxide,



such as would be demanded by Engler and Bach's interpretation of combustion phenomena, was found in my experiments.

Dry air was slowly passed for 8 hours over 20 grams of sodium benzylate in a distilling flask, kept in a bath at 45°–55°. During the first 5 hours oxidation took place with noticeable evolution of heat. Finally, dry oxygen was passed over the mixture for 10 hours, at ordinary temperatures. On extracting the salt residue thoroughly with dry ether 5.7 grams of benzyl alcohol, b. p. 200°, were obtained. The salt residue, thoroughly dried, weighed 19.4 grams. By titration with standard thiosulphate, potassium iodide and sulphuric acid, the presence therein of 0.0838 gram of sodium peroxide was established.

Titration of another portion of the salt residue with normal sulphuric acid, using phenolphthalin as an indicator, proved that the total amount of sodium hydroxide present was 3.2 grams. Examination of a third portion proved that the total amount of benzoic acid present in the salt residue was 10.6 grams.

On the Behavior of Sodium Benzylate towards Benzyl Acetate, Ethyl Acetanilide, Formethylanilide, and towards Sodium Acetoaceticbenzyl Ester under Various Conditions.

On mixing sodium benzylate in a sealed tube with the dimolecular quantity of benzyl acetate, some heat evolution takes place and the mass gradually transforms itelf into a

homogeneous, viscous condition. This mixture, whether allowed to stand for 25 days at 20° or heated for 50 hours at 100°, gives only a 2 per cent yield of acetoacetic benzyl ester, according to

$$2CH_3COOCH_2C_6H_5 + NaOCH_2C_6H_5 \rightleftharpoons 2C_6H_5CH_2OH + CH_3C(ONa) : CHCOOCH_2C_6H_5.$$

This is in marked contrast to the corresponding reaction with ethyl acetate and sodium ethylate, where the equilibrium point is reached when about 36.5 per cent of sodium acetoacetic ester is formed.

Bacon has obtained entirely analogous results[1] in his experiments with benzhydrol acetate and sodium benzhydrol. Similarly, benzhydrol acetate and benzyl acetate, when treated directly or in absolute ether solution with metallic sodium, never give, under any condition yet found, more than about 1 per cent of the corresponding acetoacetic ester. In investigating the action of metallic sodium on benzyl acetate, Conrad and Hodgkinson found, to their surprise, some 25 years ago, that no trace of an acetoacetic benzyl ester is formed, whereas ethyl, butyl and amyl acetates, when treated with sodium, give relatively large yields of the corresponding acetoacetic ester. Conrad and Hodgkinson showed that mixtures of sodium and benzyl acetate remain unchanged until a temperature of 135° is reached, when suddenly a reaction takes place with violence and without hydrogen evolution, giving, among other products, benzyl hydrocinnamate.[2] Bacon has recently studied this reaction and proved that, in addition, much sodium benzylate and some dibenzyl oxide are formed.[3] It is obvious that the formation of benzyl hydrocinnamate is an alkylation phenomenon; the only point in doubt is whether this takes place through an intermediate formation of benzyl acetoacetate or whether it is due to a direct alkylation of the benzyl acetate by phenylmethylene, according to

$$C_6H_5CH< + H—CH_2COOCH_2C_6H_5 \rightleftharpoons C_6H_5CH_2CH_2COOCH_2C_6H_5.$$

[1] This Journal, 33, 79-81.
[2] Ann. Chem. (Liebig), 193, 298; 201, 166.
[3] This Journal, 33, 93-96.

Having investigated this question with especial care experimentally, I am led to the conclusion that here, as well as in the analogous experiments with benzyl propionate and butyrate, the alkylation must take place *directly, i. e.*, without intermediate formation of acetoacetic ester.

Copper Salt of Acetoacetic Benzyl Ester.—Shaklee has found[1] that acetoacetic benzyl ester is formed almost quantitatively by heating molecular proportions of benzyl alcohol and acetoacetic ester in a bath, at 160°. It is an oily liquid boiling, without decomposition, at 162°–164° (16 mm.). The ester boils with some decomposition at about 270° under ordinary pressure; it gives a blood-red coloration with ferric chloride and alcohol. Aqueous sodium hydroxide dissolves it in the cold without decomposition, whereas aqueous sodium carbonate is without effect. Treated in absolute ether solution with metallic sodium, in the form of wire, it is converted smoothly, with hydrogen evolution, into the sodium salt which separates as an insoluble, non-hygroscopic, white powder. The most characteristic derivative is the copper salt, which separates almost quantitatively as a green precipitate on adding an excess of aqueous copper acetate to an alcoholic solution of benzyl acetoacetic ester. On crystallizing the dry salt from benzene, green, feathery crystals, melting at 156°, are obtained.

0.1832 gram salt gave 0.0326 gram CuO.

0.2310 gram salt gave 0.0410 gram CuO.

0.1248 gram salt gave 0.2698 gram CO_2 and 0.0584 gram H_2O.

0.1476 gram salt gave 0.3196 gram CO_2 and 0.0637 gram H_2O.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found. I.	Found. II.
Cu	14.27	14.21	14.18
C	59.24	58.95	59.05
H	4.94	5.19	4.79

Sodium Benzylate and Benzyl Acetate.—Twenty grams of sodium benzylate and 46.1 grams (2 mols.) of benzyl ace-

[1] This Journal, 33, 80.

tate, b. p. 210°–213°, were mixed and allowed to stand at ordinary temperatures, for 25 days, in a sealed tube. Union to form a viscous, homogeneous mass took place very soon, as mentioned above. On treating with an excess of dilute sulphuric acid much oil separated, which was taken up in ether and resolved, by further treatment with aqueous sodium carbonate, into neutral and acid products; 1.7 grams of benzoic acid and 0.8 gram of tar, insoluble in boiling water, were obtained from the soda solution.

The neutral products were at first fractionated under reduced pressure; 43 grams of benzyl alcohol, containing some benzyl acetate and boiling at 200° to 210°, were obtained; in addition 4.8 grams of oil boiling at 130°–165° (20 mm.) and 2.8 grams of non-volatile tar were found. This high-boiling oil gave a strong ferric chloride reaction, and was, accordingly, treated, in alcoholic solution, with aqueous copper acetate. The precipitate obtained was crystallized from benzene, giving thus 0.6 gram of copper acetoacetic benzyl ester melting at 153°–154°.

0.2151 gram salt gave 0.0382 gram CuO.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found.
Cu	14.27	14.18

A second experiment was carried out in which the same amount of material was heated in a sealed tube, at 100°, for 50 hours, 7 hours daily. The result was practically the same as in the first case; 0.6 gram of copper acetoacetic benzyl ester, melting at 156°, was obtained.

0.4820 gram salt gave 0.0852 gram CuO.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found.
Cu	14.27	14.12

A third experiment, with 20 grams of sodium benzylate and 46.1 grams of benzyl acetate, heated in a sealed tube for 23 hours at 120°–130° and then for 9 hours at 130°–140°, gave the following result: A larger amount of neutral, high-boiling oil was obtained than in the former experiments, but no trace of benzyl acetoacetate could be detected therein by

the ferric chloride reaction, by the formation of a copper salt, or by treatment with cold, aqueous sodium hydroxide. Special experiments, described below, show that sodium acetoacetic benzyl ester is decomposed by sodium benzylate even at 100° to a very large extent into its components and completely from 120° upwards. This result, taken in connection with the observation that mixtures of sodium benzylate and benzyl acetate, under no conditions yet ascertained, give more than a 2 per cent yield of sodium acetoacetic benzyl ester, makes it certain that the formation of benzyl hydrocinnamate in my own and in Conrad and Hodgkinson's experiments must be due to a direct alkylation of benzyl acetate by phenylmethylene. The formation of benzyl hydrocinnamate or of hydrocinnamic acid from mixtures of benzyl acetate or of sodium acetoacetic benzyl ester and sodium benzylate begins noticeably at 100°, and increases rapidly in amount as the temperature is raised to 160°, whereas all traces of sodium acetoacetic benzyl ester disappear from 120° upwards.

Thus a fourth experiment with 20 grams of sodium benzylate and 23 grams of benzyl acetate (1 mol.) gave, after heating in a sealed tube, at 140°–160°, for 42 hours, 7 hours daily, the following result:

The main reaction products, neutral to sodium carbonate, fractionated under 20 mm. pressure, gave 1 gram of non-volatile tar, 19 grams of benzyl alcohol, b. p. 100°–115°, and 3.1 grams of oil boiling at 160°–200°. The high-boiling oil was shown by the usual tests to be entirely free from benzyl acetoacetate. It probably consisted of a mixture of dibenzyl oxide and of benzyl hydrocinnamate.[1] On working up the acid products, *i. e.*, those soluble in sodium carbonate, by acidifying, extracting with ether and fractionating under 25 mm. pressure, 6.5 grams of crystalline material, boiling at 100°–195°, were obtained. A heavy oil, 1.8 grams, remained in the distilling flask.

The 6.5 grams of volatile acids were separated by fractional crystallization from water into 3.1 grams of hydrocinnamic acid, m. p. 48°; 0.3 gram of cinnamic acid, m. p. 132°; and

[1] Cf. Bacon: THIS JOURNAL, 33, 95–97.

0.4 gram of benzoic acid, m. p. 121°. This was proved in the first two cases by mixing portions with known preparations and finding that the melting point remained constant, as well as by the following analytical results:

0.4022 gram hydrocinnamic acid gave 1.0586 grams CO_2 and 0.2398 gram H_2O.

	Calculated for $C_9H_{10}O_2$.	Found.
C	72.00	71.78
H	6.66	6.62

0.1996 gram cinnamic acid gave 0.5304 gram CO_2 and 0.0982 gram H_2O.

	Calculated for $C_9H_8O_2$.	Found.
C	72.97	72.47
H	5.40	5.41

The cinnamic acid is undoubtedly formed by a condensation of benzoic aldehyde—obtained from sodium benzylate by the Dumas-Stas reaction, with benzyl acetate. The 1.8 grams of non-volatile oil, mentioned above, were found to consist chiefly of tar insoluble in hot water and on working up the portion soluble in boiling water 0.15 gram of dibenzylacetic acid, m. p. 87°, which was unchanged when mixed with a known preparation, was obtained.

Sodium Benzylate and Sodium Acetoacetic Benzyl Ester.—Fifteen grams of sodium acetoacetic benzyl ester and an equimolecular amount, 9.1 grams, of sodium benzylate, were intimately mixed in a mortar and then heated in a sealed tube, at 100°, for 100 hours, 10 hours daily. The tube was opened from time to time and some pressure, probably due to hydrogen, was noticed at first. On pouring into an excess of dilute sulphuric acid, separating into neutral and acid products, by means of sodium carbonate, etc., 6.6 grams of benzyl alcohol, b. p. 110°–150° (50 mm.), and 7.5 grams of oil, b. p. 150°–170° (20 mm.), were obtained. On treating the combined oils, in alcoholic solution, with aqueous copper acetate, 4 grams of copper acetoacetic benzyl ester, m. p. 156°, were obtained.

Only 0.5 gram of benzoic acid and no other acid could be found in the sodium carbonate solution.

A repetition of the experiment, using 15 grams of sodium acetoacetic benzyl ester and twice as much sodium benzylate, 18.2 grams, gave, after heating for 100 hours, at 100°, relatively more benzyl alcohol, 15 grams, and less high-boiling oil, 3.3 grams. The latter, however, contained only traces of acetoacetic benzyl ester and must, therefore, have consisted mainly of benzyl hydrocinnamate and dibenzyl oxide. This is also shown by the fact that on working up the sodium carbonate solution 0.5 gram of cinnamic acid, m. p. 132°, and 2 grams of hydrocinnamic acid, m. p. 48°, were obtained. In addition, some acetone was found in the original acidified aqueous solution after separating the insoluble oils.

In another experiment where an intimate mixture of 15 grams of sodium acetoacetic benzyl ester and 9.1 grams of sodium benzylate was heated in a sealed tube for 100 hours, 10 hours daily, at 150°–160°, 2 grams of pure hydrocinnamic acid and 0.7 gram of cinnamic acid were obtained. Finally, an experiment with 15 grams of sodium acetoacetic benzyl ester and 18.2 grams of sodium benzylate gave, after heating for 100 hours, at 150°–160°, etc., 7.5 grams of benzyl alcohol and 1 gram of high-boiling neutral oil, b. p. 120°–220° (25 mm.), which was found to be entirely free from acetoacetic ester. More acetone was found in this experiment than in the former ones. The sodium carbonate solution gave 0.4 gram of benzoic acid and 4.1 grams of pure hydrocinnamic acid, m. p. 48.

0.2308 gram hydrocinnamic acid gave 0.6098 gram CO_2 and 0.1368 gram H_2O.

	Calculated for $C_9H_{10}O_2$.	Found.
C	72.00	72.05
H	6.66	6.58

Finally, brief mention is made here of the fact that an intimate mixture of 33 grams of sodium benzylate and 41.6 grams of benzyl propionate gave, after heating in a sealed tube,

for 100 hours, at 150°–160°, 1.8 grams of α-methylcinnamic acid, m. p. 79°.

0.1116 gram substance gave 0.3054 gram CO_2 and 0.0648 gram H_2O.

	Calculated for $C_{10}H_{10}O_2$.	Found.
C	74.74	74.63
H	6.17	6.35

Sodium Benzylate and Ethyl Acetanilide.—Twenty-four and nine-tenths grams of sodium benzylate (1.25 mols.) and 50 grams (2 mols.) of ethyl acetanilide, heated for a short time at 100°, in a sealed tube, were transformed into a homogeneous, viscous liquid and then heated 30 hours longer at that temperature. On pouring into an excess of dilute sulphuric acid and working up as is usual, for basic, acid and neutral products, 25 grams of ethyl aniline were obtained. The neutral portion gave, on fractionation (20 mm.), 10 grams of benzyl alcohol, b. p. 103°–105°, 2 grams of unchanged ethyl acetanilide, b. p. 145°–148°, and 14.1 grams of a heavy oil, boiling at 170°–210°, whose nature was not determined but which was obviously a mixture of dibenzyl oxide and benzyl hydrocinnamate. The portion soluble in aqueous sodium hydroxide contained 1.2 grams of acetic acid and 1.5 grams of acetoacetic benzyl ester, b. p. 150°–164° (20 mm.). The last-named substance gave, on treatment with aqueous copper acetate, etc., 0.4 gram of copper acetoacetic benzyl ester, m. p. 153°.

0.2648 gram substance gave 0.0462 gram CuO.

	Calculated for $C_{22}H_{22}O_6Cu$.	Found.
Cu	14.27	13.94

In a second experiment, where 20 grams of ethyl acetanilide and the monomolecular amount, 17 grams, of sodium benzylate were used, and the mixture was heated in a sealed tube for 44 hours, at 130°–150°, 13 grams of ethyl aniline and 7 grams of benzyl alcohol, b. p. 108°–110° (22 mm.), were obtained. The sodium carbonate solution contained 5.5 grams of acids boiling at 100°–170° (20 mm.). This was separated in the

usual manner, giving 3 grams of hydrocinnamic acid and 0.5 gram of cinnamic acid.

Finally, brief mention is made here of 2 experiments with equimolecular quantities of sodium benzylate and ethyl formanilide (18 grams). In the first instance the mixture was heated in sealed tubes, for 43 hours, at 130°–150°, and in the second for 70 hours, at 150°–160°. Much benzoic acid was obtained, especially in the second experiment, but no benzylformic, *i. e.*, phenylacetic acid could be detected in either case.

On the Action of Metallic Sodium on Alkyl Acetates.—The observation that ethyl acetate, when diluted with absolute ether, reacts with metallic sodium without formation of hydrogen or sodium acetoacetic ether was first made 3 years ago in this laboratory by Bacon[1] at Dr. Nef's suggestion. Shaklee[1] had previously, under similar conditions, found that benzyl acetate and benzhydrol acetate, when diluted with absolute ether, react in the cold with metallic sodium and give mainly sodium benzylate and sodium benzhydrol, respectively. Only traces of hydrogen and of an acetoacetic ester derivative could be obtained, and in both cases the presence of a substance which gave the diacetylosazone of Pechmann, m. p. 242°, on treatment with phenylhydrazine acetate, was definitely established by Shaklee. He concluded, therefore, that diacetyl was formed in this reaction. Dimethyl ketol, however, can give the same compound on treatment with this reagent, and since Nef[2] has shown that benzil reacts with sodium according to

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + 2Na \longrightarrow \begin{matrix} C_6H_5CONa \\ \| \\ C_6H_5CONa \end{matrix},$$

giving dinatroxystilbene, which is at once decomposed by water into benzoin and 2 molecules of sodium hydroxide, it was quite possible that the diacetyl first formed in the reaction might have been converted in an analogous manner, by more sodium, into dinatroxy-β-butylene, $CH_3C(ONa) : C(ONa)CH_3$, which must then give, with water, dimethyl ketol. It was possi-

[1] This Journal, 33, 77–79.
[2] Ann. Chem. (Liebig), 308, 287.

ble, therefore, that dimethyl ketol and not diacetyl was the product formed in the reaction under discussion. This became practically certain when Bouveault and Locquin,[1] about a year ago, published the results of their work on the action of metallic sodum on ethyl butyrate and caproate. They found, for example, that sodium reacts with ethyl butyrate almost quantitatively, according to

$$2C_3H_7C : O(OC_2H_5) + 4Na \rightarrow C_3H_7C(ONa) : C(ONa)C_3H_7 + 2C_2H_5ONa.$$

The product formed, dinatroxydipropylethylene, is at once decomposed by water, giving dipropyl ketol,

$$C_3H_7CH(OH)COC_3H_7.$$

It is clear from Nef's work[2] that the action of sodium on ethyl butyrate to give these end products must proceed through 5 successive stages. I now took up the study of the action of sodium on ethyl acetate in absolute ether solution and was able to confirm, in every detail, the previous observations of Bacon. When acetic ether is diluted with 7 parts of absolute ether and is then treated with metallic sodium, in wire form, not a trace of hydrogen or of sodium acetoacetic ester is formed; furthermore, exactly 2 atoms of sodium are used for every molecule of ethyl acetate taken, as demanded by the equation,

$$2CH_3COOC_2H_5 + 4Na \rightarrow CH_3C(ONa) : C(ONa)CH_3 + 2C_2H_5ONa.$$

The amount of sodium ethylate formed in the reaction was found to be exactly that demanded by the theory, but only small quantities of dimethyl ketol,

$$CH_3CH(OH)COCH_3,$$

or its monacetate, were actually obtained on treating the reaction products with dilute acids or with acetyl chloride. This is not surprising when one considers the well-known tendency of diacetyl, of acetol and of dimethyl ketol to undergo

[1] Compt. rend., 140, 1593.

[2] Ann. Chem. (Liebig), 308, 283-293; Cf. Acree: THIS JOURNAL, 29, 588.

condensation, especially in the presence of caustic alkalies and of sodium alcoholates.

Thirty grams of sodium (2 atoms) in the form of wire were suspended in 500 cc. of absolute ether and 58 grams of pure ethyl acetate were added. A white coating appeared at once on the metal and in half an hour the temperature had risen 10°. Care was taken to keep the temperature below 34° and after an hour much light, brown powder appeared which continually increased in amount. At the end of 2 days the sodium was all gone; the calculated amount of 15 per cent hydrochloric acid was then added and the ethereal layer was well washed with water. The aqueous solution, when distilled under ordinary pressure, gave 30 grams of oil boiling at 78°–88° and 25 grams boiling at 88°–95°. These 2 fractions consisted mainly of alcohol and water, but both gave, on standing in the cold with aqueous phenylhydrazine acetate, diacetylosazone, m. p. 242°. The amounts were 3 grams and 1.8 grams, respectively. The ether solution, after getting rid of the ether by distillation, gave, on similar treatment, 0.7 gram more of pure diacetylosazone. The experiments described below with acetyl chloride prove that dimethyl ketol and not diacetyl is the reaction product under the conditions employed, and special experiments with pure dimethyl ketol and aqueous phenylhydrazine acetate have shown that only about 35 per cent of the theoretical amount of diacetylosazone can be obtained after 10 days' standing in the cold. From these data I conclude that the amount of dimethyl ketol formed from the 30 grams of sodium and 58 grams of ethyl acetate mentioned above must have been 4.14 grams.

Two experiments with sodium and the equimolecular amount of ethyl acetate were carried out in absolute ether solutions to prove that no trace of hydrogen is formed in the reaction. In the one case 26 grams of sodium, 88 grams of ethyl acetate and 1 liter of ether, in the other 19.6 grams of sodium, 75 grams of ethyl acetate and 700 cc. of ether were used. The flask containing the material was connected with a gasometer containing water. The amount of gas obtained was 1571 cc. and 991 cc., respectively. It was proved by analysis

to contain no trace of hydrogen and was found to consist of a mixture of air and ether vapor. In a third experiment an extremely small amount of hydrogen was formed. These results are in entire accord with those of Bacon, who, in 5 experiments, using 176 grams of ethyl acetate and the monatomic quantity of sodium in every case, found that only traces of hydrogen and of acetoacetic ester had been formed.[1]

Estimation of the Sodium Ethylate Formed in the Reaction.—Twenty-six and one-tenth grams of sodium, 350 cc. of ether and 50 grams of ethyl acetate were allowed to stand until no more metal was present, and then 170 grams of freshly distilled benzoyl chloride were added and the mixture heated under a reversed condenser, in a bath kept at 45°–55°, for 7 hours. The oils left after filtering from the sodium chloride and distilling off the ether were fractionated (20 mm.) and the fraction boiling at 100°–120° was freed from benzoyl chloride by shaking with cold 25 per cent sodium hydroxide; 83.3 grams of ethyl benzoate, b. p. 210°, were thus finally obtained, which corresponds to 25.5 grams of ethyl alcohol. The amount demanded by the theory is 26.0 grams. It should be mentioned that after removing the benzoyl chloride and ethyl benzoate under reduced pressure, much non-volatile oil, 71 grams, remained in the distilling flask. This did not solidify, and judging from the corresponding experiments with acetyl chloride (see below), much dibenzoyloxy-β-butylene, as well as benzoyl derivatives of condensation products of diacetyl and of dimethyl ketol, may be present.

Action of Acetyl Chloride on the Mixture of Sodium Salts.—Twenty-six and one-tenth grams of sodium, suspended in the form of wire in 500 cc. of absolute ether, were treated with 50 grams of ethyl acetate. When the metal had disappeared, 95 grams of freshly distilled acetyl chloride were added slowly, taking care to shake well and to cool with running water. The mixture was allowed to stand 2 hours, water was then added and the ethereal solution well washed with aqueous sodium carbonate and then dried with calcium chloride. The ether was distilled off by means of a Glinsky apparatus and

[1] THIS JOURNAL, 33, 79.

the oil remaining then fractionated under reduced pressure. The first distillation gave the following fractions:

I. 5.8 grams, boiling at 45°–60° (30 mm.).
II. 5.5 grams, boiling at 60°–90° (20 mm.).
III. 7.8 grams, boiling at 90°–110° (18 mm.).
IV. 11.3 grams, boiling at 110°–140° (18 mm.).

Twelve grams of non-volatile, tarry oil remained in the distilling flask. It was found impossible, by further fractionation, to obtain constant boiling products; furthermore, much loss occurs in every subsequent distillation through condensation. Fraction I. was proved to consist mainly of dimethyl ketol and fraction II. of dimethyl ketol monacetate. Both of these fractions dissolve easily in water. Fractions III. and IV. are only very slightly soluble in water and give, on hydrolysis with water at 100°, acetic acid and dimethyl ketol; it is, therefore, very probable that much diacetyloxy-β-butylene, $CH_3C(OCOCH_3) : C(OCOCH_3)CH_3$, is present in these fractions.

All the fractions obtained, I.–IV., reduce Fehling's solution slowly in the cold, and rapidly on warming; treated with phenylhydrazine acetate they all give, on standing in the cold for 10 days, diacetylosazone, m. p. 242.

In order to have sufficient material for the experiments described in the following pages, more ethyl acetate was treated with sodium, acetyl chloride, etc., and the corresponding fractions obtained were then united. The result is the same whether the reaction products, after treatment with acetyl chloride, are worked up by filtration from the sodium chloride, *i. e.*, without contact with water, or by treatment with aqueous sodium carbonate. It was found necessary to prepare dimethyl ketol and also its monacetate in order to ascertain the best methods for identifying these substances. Dimethyl ketol[1] boils at 48°–50° (20 mm.); and the monacetate, which is readily made from dimethyl ketol and acetic anhydride,

[1] The best method of preparing dimethylketol is that of Vladesco, Bull. Soc. Chim. [3] 6, 407, 801, from methyl-α-chlorethyl ketone. Its preparation from the corresponding methyl-α-bromethyl ketone, which boils at 29°–30° (10 mm.), was found to be exceedingly tedious, owing to the difficulty of separation from the isomeric ethyl brommethyl ketone.

boils at 74° under the same pressure. Kling[1] states that dimethyl ketol gives a semicarbazone, m. p. 184°. I have found that space isomeric semicarbazones are formed in this case, which are difficult to separate, so that this is not a sharp method for identifying dimethyl ketol. On the other hand, dimethyl ketol monacetate gives, as I have found, a very characteristic semicarbazone. One gram of the acetate was added to a solution of 2 grams of semicarbazine hydrochloride in 5 cc. of water, previously treated with 1.3 grams of potassium carbonate. The semicarbazone separated at once as a bulky precipitate and on crystallization from 10 parts of hot water, 1.4 grams of the pure substance were obtained in white needles, melting at 162°.

0.2517 gram substance gave 51.5 cc. N at 27° and 740 mm.

0.2212 gram substance gave 46 cc. N at 29° and 743 mm.

0.1643 gram substance gave 0.2673 gram CO_2 and 0.1050 gram H_2O.

	Calculated for $CH_3CHOCOCH_3$ | $CH_3C{:}NNHCONH_2$	Found. I.	II.
C	44.86	44.34	....
H	7.00	7.15	....
N	22.49	22.69	22.70

The yield is quantitative. It was, therefore, possible to prove sharply, by means of the carbazone, that the fractions boiling at 70°–90° (20 mm.), and obtained from ethyl acetate, sodium and acetyl chloride, as described above, consist mainly of dimethyl ketol monacetate. Thus, 1.3 grams of oil, b. p. 88°–90° (30 mm.) gave, on treatment with semicarbazine, etc., 1.3 grams of semicarbazone of dimethyl ketol monacetate, melting, after one crystallization from water, at 158°.

I. 0.1823 gram substance gave 37 cc. N at 24° and 751 mm.

II. 0.1994 gram substance gave 40.5 cc. N at 26° and 751 mm.

	Calculated for $C_7H_{13}N_3O_3$	Found. I.	II.
N	22.49	22.77	22.63

In another experiment, where 7 grams of oil, b. p. 45°–70°

[1] Ann. Chim. Phys. [8], 8, 552.

(25 mm.), were heated for 18 hours, at 100°, with 10 grams of acetic anhydride and the mixture was then treated with water, extracted with ether and dried with potassium carbonate, 1.5 grams of dimethyl ketol monacetate, boiling at 73°–74° (17 mm.), were obtained. This gave 0.8 gram of semicarbazone, m. p. 162°.

0.2386 gram substance gave 48.5 cc. N at 27° and 753 mm.

	Calculated for $C_7H_{13}N_3O_3$.	Found.
N	22.49	22.87

On treating the higher boiling oils, 90°–140° (20 mm.), obtained in the reaction under consideration, with 3 parts of water in sealed tubes, for 25 hours, at 100°, they are all decomposed, giving acetic acid and dimethyl ketol. The amount of acetic acid formed was determined by treating the resulting aqueous solutions with powdered calcium carbonate and determining the amount of unaffected carbonate, as well as by weighing the calcium acetate left after distilling off the water and dimethyl ketol on a boiling water-bath (20 mm.). The amount of acetic acid found was invariably small, *i. e.*, far less than that demanded for the hydrolysis of a substance like $CH_3C(OCOCH_3)_2{:}\ C(OCOCH_3)CH_3$, for instance, but the amount of dimethyl ketol obtained in the aqueous distillate was also correspondingly small, so that one must conclude that only small amounts of diacetyldihydroxy-β-butylene can be present in the oils boiling at 90° to 140° (20 mm.); the nature of the main products present remains, therefore, undetermined.

Thus, 14.5 grams of oil boiling at 80°-120° (20 mm.), heated for 35 hours at 100°, with 45 grams of water, used up 3.55 grams of calcium carbonate and gave 6.2 grams of calcium acetate, $Ca(C_2H_3O_2)_2.H_2O$.

Four and one-tenth grams of oil, boiling at 80° to 95° (12 mm.), heated with 13 grams of water, in a sealed tube, for 25 hours, at 100°, used up 1.2 grams of calcium carbonate and gave 2.08 grams of calcium acetate. The aqueous distillate was, in this case, extracted 20 times with ether; after drying

and then distilling off the ether by means of a Glinsky apparatus, the oil remaining gave, on standing for 7 days with aqueous phenylhydrazine acetate, 0.55 gram diacetylosazone, m. p. 242°.

Finally, the following experiments with various non-hydrolyzed fractions obtained in the reaction under consideration are of interest.

One gram of oil boiling at 40°–45° (40 mm.) gave, on standing in the cold for 1 week with aqueous phenylhydrazine acetate, 0.35 gram of pure diacetylosazone. One gram of oil boiling at 45° to 70° (38 mm.) gave, on similar treatment, 1.05 grams of osazone. One gram of oil, boiling at 57° to 60° (20 mm.), gave 1.2 grams of osazone. The diacetylosazones obtained in these 3 cases were simply filtered off and washed with cold ether; they all melted constantly at 242°.

0.2681 gram substance gave 51 cc. N at 27° and 752 mm.

	Calculated for $C_{16}H_{18}N_4$.	Found.
N	21.08	21.16

One gram of oil boiling at 95° to 104° (14 mm.) gave, on similar treatment with aqueous phenylhydrazine acetate, 0.5 gram of osazone. Another fraction, one gram of oil boiling at 105° to 115° (14 mm.), gave 0.4 gram of diacetyl osazone, m. p. 242°.

0.2856 gram substance gave 54.65 cc. N at 27° and 749 mm.

	Calculated for $C_{16}H_{18}N_4$.	Found.
N	21.08	21.20

The results presented above prove decisively, therefore, that small quantities of dimethyl ketol are formed by the action of sodium on ethyl acetate when diluted with absolute ether. The major portion of the dimethyl ketol, as well as of the diacetyl, which is obviously an intermediate product in the reaction, must at once undergo further condensation. This is not surprising, in view of the well-known properties of these compounds. Finally, mention should be made of an experiment where 13.4 grams (diatomic quantity) of sodium, suspended

in the form of wire in 250 cc. of absolute ether, were treated with 25 grams of diacetyl, b. p. 87°–91°. Action took place slowly and without hydrogen evolution. The metal gradually crumbled and a reddish-brown powder took its place. At the end of one week no further action was noticeable and about one-half of the sodium remained unchanged.[1] The mixture was now treated with 35 grams of acetyl chloride, and after 2 hours' standing, was worked up by filtering from the sodium chloride and the sodium and then distilling off the ether by means of a Glinsky apparatus. On attempting to distil the oil left, 30 grams, practically nothing distilled off (25 mm.) even when the temperature of the surrounding bath had reached 200°; 27 grams of dark, viscous tar remained in the distilling flask.

In conclusion, I wish to express my thanks to Professor Nef for the inspiration and help which he has given me in this work.

THE OSMOTIC PRESSURE AND THE DEPRESSION OF THE FREEZING POINTS OF SOLUTIONS OF GLUCOSE.[2]

By H. N. Morse, J. C. W. Frazer, and B. F. Lovelace.

PART II.

In Part I. of this paper[3] we described the measures which had been taken to secure uniform temperatures in the bath in which the osmotic cell is located during an experiment, also certain improvements in apparatus and modifications of procedure which had been introduced since the earlier work[4] upon the osmotic pressure of cane sugar. We also described a difficulty encountered early in the work, which was due to the persistent infection of the cells with *penicillium*; and the efforts which were made to find an efficient poison for the fungus which could be employed without injury to the

[1] Cf. corresponding experiment of Nef with benzil, Ann. Chem. (Liebig), 308, 286-7.

[2] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution.

[3] This Journal, 36, 1.

[4] *Ibid.*, 34, 1.

membranes and without sensible effect upon the accuracy of the results.

In this part of the paper the formal measurements will be presented with only such additional matter as may be necessary to an understanding of the conditions under which they were made.

It was stated[1] that the difficulty of preparing non-permeable membranes increases as the molecular weights of the substances diminish, and that a membrane which is not sensibly permeable to cane sugar may leak glucose. Except in one instance, only two cells, "A" and "D," were employed for the present measurements because, of the half dozen cells now in use, they were the most readily brought into fit condition[2] for the work. "A" has been long in service[3] and had developed such slowness in reaching maximum pressures that it was subjected early in the work to a process of renovation. This "renovation" is resorted to whenever the wall of a cell becomes so filled with membrane material that the passage of water through it is intolerably slow, and also when there is reason to suspect that the junction[4] between the glass tube and the soapstone ring, or that between the ring and the cell wall, has become defective. The process consists in opening the cell by digging out the cement, and in removing the membrane by soaking the cell successively in a warm solution of an alkaline tartrate, in water, in hydrochloric acid, and finally again in water. To remove any soluble matter still remaining in the wall, the cell is placed in dilute hydrochloric acid, which is electrolyzed with the cell wall between the poles. The acid is replaced by water—with frequent renewals of the latter—and the electrolysis is continued until the conductivity is reduced to about that of the distilled water. Finally, the cell is reburned at a temperature of 900° or 1000° and is thereafter treated in every respect like a new cell[5].

In A, solutions of all concentrations developed their maxi-

[1] THIS JOURNAL, 36, 33.
[2] *Ibid.*, 36, 30.
[3] *Ibid.*, 36, 54.
[4] *Ibid.*, 34, 11.
[5] *Ibid.*, 34, 11; 36, 30.

mum pressures continuously and maintained them for long periods, showing that the membrane did not leak. The conduct of D, in this respect, was also satisfactory except in one or two instances, where, after having reached a maximum, the pressure exhibited a slight tendency to decline, suggesting either that the membranes, on those occasions, were not wholly impervious to the glucose, or that some of the joints of the cell had become slightly defective. D was accordingly withdrawn for "renovation" and the work was finished with A. The cell G, which was employed for a single measurement (Table XVI.), likewise exhibited an inability to maintain a maximum pressure for a long period, and it was withdrawn for renovation and for subsequent use in the measurement of the pressure of cane sugar solutions at 0°.

The preparation of the manometers has been described in sufficient detail elsewhere,[1] and the only additional fact concerning them which should be recorded here relates to the possible gradual reduction of the air volumes through the action of the oxygen on the impurities in the mercury. To prepare the mercury for manometric purposes, it was sprayed daily for 3 weeks, according to the method of Lothar Meyer, through 1.75 meter columns of solutions of ferric chloride, hydrochloric acid, and nitric acid, and then preserved under concentrated sulphuric acid. Notwithstanding this thorough treatment of the mercury, the air volumes in our manometers have sensibly diminished in the course of time, especially in those which have been frequently used for the measurement of the higher pressures. According to the last verifications the diminution in the manometers most frequently employed in the present work (numbers 5, 6, 11, and 13) has amounted respectively to 1.66, 1.29, 1.68, and 1.80 per cent of the original air volumes. It is hardly necessary to state that appropriate corrections have been applied for this diminution of the air volumes. In the future, the mercury which is to be used in manometers will be prepared from the pure oxide and the instruments will be filled with nitrogen instead of air.

[1] THIS JOURNAL, 34, 3; 36, 30.

It was stated in Part I. of this paper[1] that an effective remedy for *penicillium* had been found in extremely dilute solutions of thymol, also that the same solutions retarded, in a marked degree, the alcoholic fermentation which must be carefully guarded against in all experiments with glucose. Hence all liquids used in the present work—the sugar solutions, the liquid in which the cells are immersed during an experiment, and the water in which they are soaked at all times when not in use—have been made 0.001 weight-normal with respect to thymol. There has been no reappearance of *penicillium*, nor have we observed at any time any indication of alcoholic fermentation in the solutions of glucose.

In the tables which follow, the rotation (in saccharimeter degrees) of the solution, before and after a measurement, is given. It will be noticed that in all cases, except two, the rotation was less at the close of an experiment than in the beginning, indicating a dilution of the solution while in the cell, and that a correction has been made for this dilution in each case. The causes of the observed dilution of the solutions while in the cells have been amply discussed in former papers[2] but the importance of the subject justifies a re-enumeration of them. They are, (1) the distension of the cell under pressure; (2) the entrance into the manometer of a volume of the liquid equal to the diminution of the air volume; (3) the pushing upwards of the manometer through the stopper; (4) the upward displacement of the material of the stopper; (5) the sucking in of water from the cell wall by the solution while the cell is being closed at the beginning, and opened at the end of an experiment; (6) fermentation (which would cause a loss of rotation); and, finally, (7) leakage of the membrane.

The ability of the membranes employed in this work to maintain *maximum* pressures for long periods was demonstrated before the formal measurements here recorded were undertaken, and whenever a cell showed itself at all defective in this respect it was withdrawn.

The more important sources of dilution of the cell contents

[1] THIS JOURNAL, **36**, 34.
[2] *Ibid.*, **36**, 26, 48.

are to be looked for among the causes enumerated under 3, 4 and 5, namely, the pushing, upward of the manometer, the upward displacement of the material of the stopper, and the sucking in of water from the cell wall. Of the three, the last is believed to have had the greatest effect in bringing about a dilution of the glucose solutions while in the cells.

The amount of dilution due to distortion of the stopper and the sucking in of water cannot be ascertained, but that due to upward displacement of the manometer is easily calculated. The following table—giving the results of a few such calculations—will show that it is not, as a rule, the principal cause of dilution:

Table I.

Weight-normal concentration.	Number of experiment.	Upward displacement of manometer. mm.	Amount of dilution. Percentage.	Dilution due to displacement of manometer. Percentage.
0.3	2	0.52	0.64	0.07
0.5	2	0.57	1.16	0.08
0.6	1	7.29	3.76	0.94
"	3	0.76	0.32	0.11
0.7	2	3.24	2.82	0.21
"	3	6.11	1.69	0.84
0.8	1	9.82	2.76	1.42
"	2	2.11	1.74	0.30
"	3	2.12	1.74	0.30
0.9	1	2.57	1.45	0.35
"	2	0.98	1.00	0.12
"	3	1.69	0.66	0.23
1.0	1	1.49	0.91	0.20
"	2	1.56	0.91	0.14
"	3	1.24	1.72	0.17

When all loss of rotation in the contents of the cell is ascribable to *dilution*, as in the case of glucose, the difficulty is not a serious one; but when, as in the case of cane sugar, it is due partly to *dilution* and partly to *inversion*, it becomes highly important to eliminate, or at least to reduce to insignificance, the dilution factor. With this end in view, we have in process of construction a new form of cell which, it is hoped, will enable us to dispense with rubber stoppers and which can be

much more expeditiously closed and opened than the cells we are now using.

The material of which the glucose solutions were made is that known as "*Traubenzucker Kahlbaum.*" It was pulverized, placed over calcium chloride and freely aerated by means of a current of dried air in order to hasten the removal of the odor of alcohol. After this treatment the material did not sensibly lose in weight when heated to a higher temperature in an air-bath. It melted quite sharply at 146°. Two determinations of carbon and hydrogen gave 40.03 and 40.04, instead of 39.98 per cent for the former, and 6.84 and 6.83 instead of 6.71 per cent for the latter.

The more important details of the individual measurements which are contained in Tables II. to XXVI., inclusive, are brought together in Table XXVII., which gives for each experiment: (1) the temperatures of the bath-mean, highest, and lowest; (2) the observed osmotic pressure-mean, highest, and lowest; (3) the calculated pressure-mean, highest, and lowest, if molecular-equivalent quantities of a gas are confined within the volume of the solvent at the same temperatures; (4) the differences, expressed in fractions of an atmosphere, between the mean osmotic and the mean calculated gas pressure; (5) the molecular weight of glucose—mean, highest and lowest—calculated from the observed osmotic pressures; and, finally, (6) the mean molecular weights for each concentration.

Table XXVIII. contains only the mean temperatures, the mean osmotic and the calculated gas pressures and their differences, and the mean calculated molecular weights.

A general view of the results is most readily obtained by an inspection of Table XXVIII., while an independent judgment of the weight to be attached to any individual determination can be arrived at by tracing it backwards through Table XXVII. to that in which the details of the measurement are given.

In order to facilitate a comparison of the results for glucose with those earlier obtained for cane sugar, two other tables (Nos. XXIX. and XXX.) have been introduced. They

Table II.

Original wt. normal concentration of solution, 0.1. Experiment No. 1.
Rotation of original solution, 5°.4. Manometer used, No. 11.
Rotation at conclusion of experiment, 5°.2. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 3.70 per cent. Cell used, D.
Calibration units of air in manometer, 473.77. Resistance of membrane, 65,000 ohms.
Time of setting up cell, 4.30 P.M., April 18, 1906. Initial pressure.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
April 19												
11.00 A.M.	23°.5	22°.8	185.28									
2.00 P.M.	23°.5	23°.1	185.08									
4.30 P.M.	23°.5	23°.4	185.03									
April 20												
9.00 A.M.	23°.6	23°.4	185.06									
5.30 P.M.	23°.7	24°.5	184.70									
April 21												
11.00 A.M.	24°.0	24°.5	181.46									
3.00 P.M.	24°.1	24°.6	181.00	166.01	0.99	0.36	0.09	0.02	2.33	2.42	—0.09	
April 22												
11.00 A.M.	24°.3	24°.1	179.01	164.46	0.99	0.36	0.09	0.02	2.36	2.43	—0.07	
6.00 P.M.	24°.4	23°.9	178.77	164.35	0.99	0.36	0.09	0.02	2.37	2.43	—0.06	
April 23												
4.00 P.M.	24°.1	22°.8	177.48	163.77	0.99	0.36	0.09	0.02	2.38	2.42	—0.04	182.0
April 24												
10.00 A.M.	23°.9	23°.4	176.42	162.46	0.99	0.36	0.09	0.02	2.39	2.42	—0.03	181.1
3.00 P.M.	23°.9	23°.5	176.46	162.45	0.99	0.36	0.09	0.02	2.39	2.42	—0.03	181.1

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 181.4

Table III.

Original wt. normal concentration of solution, 0.1. Experiment No. 2.
Rotation of original solution, 5°.4. Manometer used, No. 13.
Rotation at conclusion of experiment, 5°.4. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.0 per cent. Cell used, D.
Calibration units of air in manometer, 442.92. Resistance of membrane, 115,000 ohms.
Time of setting up cell, 12.00 M., May 29, 1906. Initial pressure, 1.9 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							Mol. Wt. calculated from osmotic pressure.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	
May 29												
2.30 P.M.	25°.6	24°.7	153.67									
4.45 P.M.	25°.6	24°.8	154.92									
May 30												
9.30 A.M.	25°.4	24°.4	159.60									
4.30 P.M.	25°.2	24°.6	162.46									
May 31												
10.00 A.M.	25°.1	24°.5	164.98	151.37	1.00	0.47	0.00	0.02	2.41	2.43	—0.02	180.3
5.30 P.M.	25°.0	25°.5	165.44	151.28	1.00	0.47	0.00	0.02	2.42	2.43	—0.01	179.5
June 1												
10.00 A.M.	25°.2	25°.1	165.22	151.28	1.00	0.47	0.00	0.02	2.42	2.43	—0.01	179.7

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 179.83

Table IV.

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
Rotation of original solution, 10°.6. Manometer used, No. 8.
Rotation at conclusion of experiment, 10°.5. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.94 per cent. Cell used, D.
Calibration units of air in manometer, 441.97. Resistance of membrane, 94,000 ohms.
Time of setting up cell, 5.00 P.M., April 26, 1906. Initial pressure.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
April 27												
11.00 A.M.	22°.9	23°.2	94.18									
4.00 P.M.	22°.9	23°.7	94.42									
April 28												
11.00 A.M.	23°.3	24°.1	94.77									
April 29												
10.00 A.M.	23°.6	23°.3	94.74									
April 30												
10.00 A.M.	23°.6	24°.1	94.79									
5.00 P.M.	23°.7	24°.1	94.70									
May 1												
9.00 A.M.	24°.0	24°.3	94.44	86.71	1.00	0.59	0.05	0.02	4.75	4.85	—0.10	182.3
3.00 P.M.	24°.0	24°.1	94.42	86.74	1.00	0.59	0.05	0.02	4.75	4.85	—0.10	182.3
May 2												
11.00 A.M.	24°.2	24°.3	94.36	86.63	0.99	0.59	0.05	0.02	4.79	4.85	—0.06	180.7

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 181.77

Table V.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 10°.6.
Rotation at conclusion of experiment, 10°.5.
Percentage loss in concentration, 0.94 per cent.
Calibration units of air in manometer, 473.77.
Time of setting up cell, 4.15 P.M., May 3, 1906.

Experiment No. 2.
Manometer used, No. 11.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 91,000 ohms.
Initial pressure.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 3												
9.00 P.M.	24°.9	25°.4	100.89									
May 4												
9.00 A.M.	24°.9	24°.7	98.73									
5.00 P.M.	24°.9	24°.9	99.18									
May 5												
10.00 A.M.	25°.0	24°.9	99.32									
May 6												
10.30 A.M.	25°.2	25°.3	99.17	90.74	0.99	0.47	0.05	0.02	4.77	4.86	—0.09	182.3
May 7												
10.00 A.M.	25°.1	24°.3	98.90	90.80	1.00	0.47	0.05	0.02	4.76	4.86	—0.10	182.6
May 8												
12.00 M.	24°.7	23°.9	98.43	90.49	1.00	0.47	0.05	0.02	4.77	4.86	—0.09	181.9
2.30 P.M.	24°.7	24°.1	98.43	90.43	1.00	0.47	0.05	0.02	4.78	4.86	—0.08	181.6

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 182.10

Table VI.

Original wt. normal concentration of solution, 0.3. Experiment No. 1.
Rotation of original solution, 15°.7. Manometer used, No. 11.
Rotation at conclusion of experiment, 15°.7. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.00 per cent. Cell used, D.
Calibration units of air in manometer, 473.77. Resistance of membrane, 108,000 ohms.
Time of setting up cell, 4.15 P.M., May 10, 1906. Initial pressure, 5.9 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 11												
11.00 A.M.	22°.2	21°.9	67.19	62.19	1.00	0.51	0.00	0.02	7.15	7.22	—0.07	180.5
2.30 P.M.	22°.2	22°.0	67.28	62.25	1.00	0.51	0.00	0.02	7.14	7.22	—0.08	180.8
5.00 P.M.	22°.3	22°.6	67.81	62.61	1.00	0.51	0.00	0.02	7.10	7.22	—0.12	181.9
May 12												
10.00 A.M.	22°.2	22°.1	67.83	62.73	1.00	0.51	0.00	0.02	7.08	7.22	—0.14	182.3

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 181.38

Table VII.

Original wt. normal concentration of solution, 0.3.
Rotation of original solution, 15°.7.
Rotation at conclusion of experiment, 15°.6.
Percentage loss in concentration, 0.64 per cent.
Calibration units of air in manometer, 473.77.
Time of setting up cell, 4.30 P.M., May 14, 1906.

Experiment No. 2.
Manometer used, No. 11.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 91,000 ohms.
Initial pressure, 5.9 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 14												
10.40 P.M.	23°.3	24°.8	68.65	62.92	1.01	0.51	0.05	0.02	7.10	7.25	—0.15	
May 15												
9.00 A.M.	23°.5	24°.1	67.67	62.17	1.01	0.51	0.05	0.02	7.19	7.25	—0.06	180.3
2.30 P.M.	23°.5	23°.8	67.73	62.29	1.01	0.51	0.05	0.02	7.17	7.25	—0.08	180.8
May 16												
3.30 P.M.	23°.6	23°.7	67.95	62.51	1.00	0.51	0.05	0.02	7.16	7.26	—0.10	181.1

Displacement of manometer = 0.52 mm.
Dilution due to displacement of manometer = 0.07 per cent. Mean Mol. Wt. 180.73
H = 1 Mol. Wt. Glucose = 178.74.

Table VIII.

Original wt. normal concentration of solution, 0.4. Experiment No. 1.
Rotation of original solution, 20°.8. Manometer used, No. 13.
Rotation at conclusion of experiment, 20°.7. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.48 per cent. Cell used, D.
Calibration units of air in manometer, 442.92. Resistance of membrane, 97,000.
Time of setting up cell, 4.30 P.M., May 22, 1906. Initial pressure, 5.7 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 23												
10.00 A.M.	27°.0	26°.1	48.28	44.06	1.01	0.61	0.05	0.02	9.72	9.79	—0.07	179.99
12.00 M.	26°.9	26°.2	48.36	44.12	1.01	0.61	0.05	0.02	9.71	9.78	—0.07	179.83
3.00 P.M.	26°.8	26°.3	48.61	44.35	1.01	0.61	0.05	0.02	9.67	9.78	—0.11	180.80

H = 1 Mol. Wt. Glucose = 178.74. Mean Mol. Wt. 180.21

Table IX.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.8.
Rotation at conclusion of experiment, 20°.7.
Percentage loss in concentration, 0.48 per cent.
Calibration units of air in manometer, 442.92.
Time of setting up cell, 4.30 P.M., May 25, 1906.

Experiment No. 2.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, D.
Resistance of membrane, 98,000 ohms.
Initial pressure, 9.36 atmospheres.

Time. May 26	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
9.00 A.M.	26°.6	26°.5	48.67	44.35	0.99	0.61	0.05	0.02	9.67	9.77	—0.10	180.69
12.00 M.	26°.6	26°.6	48.77	44.43	0.99	0.61	0.05	0.02	9.66	9.77	—0.11	180.88
3.30 P.M.	26°.7	27°.0	48.97	44.55	0.99	0.61	0.05	0.02	9.63	9.78	—0.15	181.49

H = 1 Mol. Wt. Glucose = 178.74. Mean Mol. Wt. 181.02

Table X.

Original wt. normal concentration of solution, 0.5. Experiment No. 1.
Rotation of original solution, 25°.8. Manometer used, No. 14.
Rotation at conclusion of experiment, 25°.3. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.94 per cent. Cell used, A.
Calibration units of air in manometer, 467.21. Resistance of membrane, 184,660 ohms.
Time of setting up cell, 5.30 P.M., Jan. 22, 1906. Initial pressure.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Jan. 22												
9.00 P.M.	21°.20	...	78.01									
Jan. 23												
9.00 A.M.	21°.40	23°.1	42.81									
12.30 P.M.	21°.45	23°.4	42.31									
3.00 P.M.	21°.60	23°.4	42.15									
5.00 P.M.	21°.62	23°.4	41.96									
8.30 P.M.	21°.70	23°.4	41.78									
Jan. 24												
9.10 A.M.	21°.85	22°.2	41.35									
1.00 P.M.	21°.90	22°.7	41.37									
3.00 "	21°.90	22°.6	41.39	38.22	1.01	0.60	0.23	0.02	12.06	12.03	+0.03	178.25
5.00 "	21°.90	22°.8	41.38	38.18	1.01	0.60	0.23	0.02	12.07	12.03	+0.04	178.10
9.00 "	21°.75	22°.4	41.42	38.27	1.01	0.60	0.23	0.02	12.05	12.02	+0.03	178.31
Jan. 25												
9.15 A.M.	21°.90	22°.3	41.29	38.16	1.02	0.60	0.23	0.02	12.09	12.03	+0.06	177.81

H = 1 Mol. Wt. Glucose = 178.74. Mean Mol. Wt. 178.12

Table XI.

Original wt. normal concentration of solution, 0.5. Experiment No. 2.
Rotation of original solution, 25°.8. Manometer used, No. 8.
Rotation at conclusion of experiment, 25°.5. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.16 per cent. Cell used, D.
Calibration units of air in manometer, 441.97. Resistance of membrane, 98,000.
Time of setting up cell, 12.30 P.M., May 17, 1906. Initial pressure, 10 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
May 17												
11.30 P.M.	23°.8	25°.7	39.78	36.35	1.00	0.66	0.14	0.02	11.98	12.10	—0.12	180.59
May 18												
9.00 A.M.	24°.2	25°.6	39.63	36.22	1.00	0.66	0.14	0.02	12.02	12.12	—0.10	180.24
5.00 P.M.	24°.5	26°.6	39.89	36.34	0.99	0.66	0.14	0.02	11.99	12.13	—0.14	180.87

Displacement of manometer = 0.57 mm. Mean Mol. Wt. 180.57

Dilution due to displacement of manometer = 0.08 per cent.

H = 1 Mol. Wt. Glucose = 178.74.

Table XII.

Original wt. normal concentration of solution, 0.6. Experiment No. 1.
Rotation of original solution, 30°.6. Manometer used, No. 14.
Rotation at conclusion of experiment, 29°.45. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 3.76 per cent. Cell used, A.
Calibration units of air in manometer, 467.21. Resistance of membrane.
Time of setting up cell, 5.30 P.M., Jan. 25, 1906. Initial pressure, 7.0 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Jan. 25												
9.00 P.M.	21°.96	22°.72	47.71									
Jan. 26												
9.15 A.M.	22°.2	22°.65	37.27									
3.40 P.M.	22°.2	22°.70	36.61									
5.00 "	22°.2	22°.80	36.62									
8.30 "	22°.2	22°.80	36.44									
Jan. 27												
10.30 A.M.	22°.2	22°.80	35.94									
3.00 P.M.	22°.2	22°.82	35.75									
4.45 "	22°.2	23°.00	35.76									
9.00 "	22°.2	22°.90	35.61									
Jan. 28												
12.00 M.	22°.3	22°.80	35.39	32.66	0.99	0.63	0.54	0.02	14.47	14.43	+0.04	178.52
8.00 P.M.	22°.7	22°.80	35.13	32.42	0.99	0.63	0.54	0.02	14.59	14.47	+0.12	177.39
Jan. 29.												
9.00 A.M.	22°.7	22°.75	35.06	32.36	1.00	0.63	0.54	0.02	14.62	14.47	+0.15	176.95

Displacement of manometer = 7.29 mm.
Dilution due to displacement of manometer = 0.94 per cent. Mean Mol. Wt. 177.62
H = 1 Mol. Wt. Glucose = 178.74.

Table XIII.

Original wt. normal concentration of solution, 0.6. Experiment No. 2.
Rotation of original solution, 30°.6. Manometer used, No. 14.
Rotation at conclusion of experiment, 30°.0. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.96 per cent. Cell used, A.
Calibration units of air in manometer, 467.21. Resistance of membrane, 68,250 ohms.
Time of setting up cell, 5.30 P.M., Feb. 1, 1906. Initial pressure, 6.5 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Feb. 1												
8.15 P.M.	22°.40	23°.40	48.23									
Feb. 2												
9.00 A.M.	22°.40	23°.36	36.55									
3.00 P.M.	22°.42	23°.36	35.95									
8.30 "	22°.43	22°.58	35.48									
Feb. 3												
9.00 A.M.	22°.45	22°.58	35.08	32.42	1.01	0.63	0.28	0.02	14.31	14.40	—0.09	180.60
3.00 P.M.	22°.45	22°.42	35.08	32.41	1.01	0.63	0.28	0.02	14.31	14.40	—0.09	180.60
9.00 P.M.	22°.35	22°.46	35.08	32.41	1.01	0.63	0.28	0.02	14.31	14.39	—0.08	180.54
Feb. 4												
10.00 A.M.	22°.35	22°.40	34.95	32.30	1.01	0.63	0.28	0.02	14.36	14.39	—0.03	179.92

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 180.42

Table XIV.

Original wt. normal concentration of solution, 0.6. Experiment No. 3.
Rotation of original solution, 30°.7. Manometer used, No. 5.
Rotation at conclusion of experiment, 30°.6. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.32 per cent. Cell used, D.
Calibration units of air in manometer, 434.98. Resistance of membrane, 108,000 ohms.
Time of setting up cell, 12.15 P.M., Oct. 13, 1906. Initial pressure, 10.46 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Oct. 13												
3.30 P.M.	22°.3	22°.5	35.30									
10.00 "	22°.3	22°.3	32.17	29.73	1.01	0.64	0.04	0.02	14.32	14.45	—0.13	180.39
Oct. 14												
10.00 A.M.	22°.3	22°.2	32.24	29.81	1.01	0.64	0.04	0.02	14.28	14.45	—0.17	180.89
1.00 P.M.	22°.4	22°.5	32.33	29.86	1.01	0.64	0.04	0.02	14.26	14.46	—0.20	181.21

Displacement of manometer = 0.76 mm.
Dilution due to displacement of manometer = 0.11 per cent. Mean Mol. Wt. 180.83
H = 1 Mol. Wt. Glucose = 178.74

Table XV.

Original wt. normal concentration of solution, 0.7. Experiment No. 1.
Rotation of original solution, 35°.5. Manometer used, No. 14.
Rotation at conclusion of experiment, 34°.6. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 2.54 per cent. Cell used, A.
Calibration units of air in manometer, 467.21. Resistance of membrane, 110,600 ohms.
Time of setting up cell, 5.00 P.M., Feb. 5, 1906. Initial pressure, 5 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Feb. 5												
9.00 P.M.	22°.31	22°.71	38.08									
Feb. 6												
10.00 A.M.	22°.32	22°.30	30.60									
3.00 P.M.	22°.32	22°.56	30.36									
5.00 "	22°.34	22°.58	30.37									
8.00 "	22°.26	22°.22	30.29									
Feb. 7												
9.00 A.M.	22°.32	22°.53	30.20	27.89	1.01	0.62	0.43	0.02	16.81	16.86	—0.05	179.28
12.00 M.	22°.25	22°.66	30.19	27.87	1.01	0.62	0.43	0.02	16.82	16.85	—0.03	179.14
5.00 P.M.	22°.20	22°.46	30.17	27.87	1.01	0.62	0.43	0.02	16.82	16.85	—0.03	179.11

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 179.18

Table XVI.

Original wt. normal concentration of solution, 0.7. Experiment No. 2.
Rotation of original solution, 35°.5. Manometer used, No. 11.
Rotation at conclusion of experiment, 34°.5. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 2.82 per cent. Cell used, G.
Calibration units of air in manometer, 473.77. Resistance of membrane, 218,000 ohms.
Time of setting up cell, 4.15 P.M., June 1, 1906. Initial pressure, 14 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							Mol. Wt. calculated from osmotic pressure.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	
June 1												
6.20 P.M.	25°.2	25°.9	30.58									
7.30 "	25°.2	25°.9	30.14									
9.00 "	25°.3	25°.8	30.15									
June 2												
10.00 A.M.	25°.3	25°.4	30.45	27.85	1.00	0.56	0.47	0.02	17.06	17.03	+0.03	178.45
2.30 P.M.	25°.4	26°.2	30.70	28.01	1.00	0.56	0.47	0.02	16.96	17.04	—0.08	179.56
5.30 P.M.	25°.4	26°.4	30.73	28.02	1.00	0.56	0.47	0.02	16.96	17.04	—0.08	179.56
June 3												
10.30 A.M.	25°.6	25°.9	30.85	28.17	1.00	0.56	0.47	0.02	16.87	17.05	—0.18	180.61

Displacement of manometer = 3.24 mm.
Dilution due to displacement of manometer = 0.21 per cent Mean Mol. Wt. 179.55
H = 1 Mol. Wt. Glucose = 178.74.

Table XVII.

Original wt. normal concentration of solution, 0.7. Experiment No. 3.
Rotation of original solution, 35°.5. Manometer used, No. 5.
Rotation at conclusion of experiment, 34°.9. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.69 per cent. Cell used, A.
Calibration units of air in manometer, 434.98. Resistance of membrane, 110,000 ohms.
Time of setting up cell, 4.30 P.M., Nov. 12, 1906. Initial pressure, 11.7 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Nov. 12												
9.00 P.M.	22°.7	22°.8	31.41									
Nov. 13												
10.00 A.M.	22°.7	22°.7	29.51									
2.30 P.M.	22°.7	22°.6	28.88									
4.30 "	22°.7	22°.6	28.77									
8.30 "	22°.7	22°.7	28.58									
Nov. 14												
10.00 A.M.	22°.7	22°.5	28.01	25.87	1.00	0.64	0.28	0.02	16.75	16.88	—0.13	180.16
1.00 P.M.	22°.7	22°.7	28.05	25.89	1.00	0.64	0.28	0.02	16.74	16.88	—0.14	180.27
3.30 "	22°.7	22°.9	28.03	25.85	1.00	0.64	0.28	0.02	16.76	16.88	—0.12	180.06

Displacement of manometer = 6.11 mm.

Dilution due to displacement of manometer = 0.84 per cent. Mean Mol. Wt. 180.16

H = 1 Mol. Wt. Glucose = 178.74.

Table XVIII.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
Rotation of original solution, 40°.2. Manometer used, No. 5.
Rotation at conclusion of experiment, 39°.1. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 2.76 per cent. Cell used, A.
Calibration units of air in manometer, 434.98. Resistance of membrane, 111,000 ohms.
Time of setting up cell, 4.00 P.M., Nov. 15, 1906. Initial pressure, 7.2 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Nov. 15												
8.30 P.M.	22°.8	22°.9	41.21									
11.45 "	22°.8	22°.8	27.63									
Nov. 16												
10.00 A.M.	22°.9	22°.7	25.10									
1.00 P.M.	22°.9	22°.9	25.07									
3.30 "	22°.9	22°.9	24.99									
7.30 "	22°.8	22°.9	24.94	23.00	1.00	0.64	0.53	0.02	19.10	19.30	—0.20	
Nov. 17												
10.30 A.M.	23°.0	22°.9	24.73	22.81	1.00	0.64	0.53	0.02	19.26	19.31	—0.05	179.25
2.30 P.M.	23°.0	23°.2	24.74	22.79	1.00	0.64	0.53	0.02	19.28	19.31	—0.03	179.06

Displacement of manometer = 9.82 mm.
Dilution due to displacement of manometer = 1.42 per cent. Mean Mol. Wt. 179.16
H = 1 Mol. Wt. Glucose = 178.74.

Table XIX.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, 40°.2.
Rotation at conclusion of experiment, 39°.5.
Percentage loss in concentration, 1.74 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.15 P.M., Nov. 19, 1906.

Experiment No. 2.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 108,000 ohms.
Initial pressure, 12.8 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Nov. 19												
9.45 P.M.	22°.9	23°.9	26.56									
Nov. 20												
10.30 A.M.	23°.0	23°.1	25.26									
1.00 P.M.	23°.0	23°.5	25.21									
4.15 "	23°.1	23°.8	25.10									
Nov. 21												
10.00 A.M.	23°.1	22°.7	24.79									
2.15 P.M.	23°.1	23°.3	24.77	22.82	1.00	0.64	0.34	0.02	19.06	19.32	—0.26	
4.30 "	23°.1	23°.7	24.72	22.74	1.00	0.64	0.34	0.02	19.13	19.32	—0.19	180.53
Nov. 22												
10.00 A.M.	23°.4	23°.6	24.67	22.70	1.00	0.64	0.34	0.02	19.16	19.34	—0.18	180.43
12.00 M.	23°.5	23°.9	24.65	22.66	1.00	0.64	0.34	0.02	19.19	19.35	—0.16	180.21

Displacement of manometer = 2.11 mm.

Dilution due to displacement of manometer = 0.30 per cent. Mean Mol. Wt. 180.39

H = 1 Mol. Wt. Glucose = 178.74.

Table XX.

Original wt. normal concentration of solution, 0.8. Experiment No. 3.
Rotation of original solution, 40°.2. Manometer used, No. 6.
Rotation at conclusion of experiment, 39°.5. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.74 per cent. Cell used, A.
Calibration units of air in manometer, 396.89. Resistance of membrane, 155,000.
Time of setting up cell, 4.30 P.M., Nov. 23, 1906. Initial pressure, 12.1 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Nov. 23												
7.30 P.M.	23°.6	23°.6	24.73									
Nov. 24												
4.20 A.M.	23°.6	23°.3	22.81									
11.00 "	23°.6	23°.1	22.61									
3.00 P.M.	23°.6	23°.6	22.71									
Nov. 25												
10.30 A.M.	23°.7	23°.1	22.44	20.68	1.00	0.67	0.34	0.02	19.22	19.36	—0.14	180.05
3.00 P.M.	23°.6	23°.4	22.45	20.67	1.00	0.67	0.34	0.02	19.23	19.35	—0.12	179.89
9.30 P.M.	23°.7	23°.4	22.42	20.64	1.00	0.67	0.34	0.02	19.26	19.36	—0.10	179.67
Nov. 26												
10.45 A.M.	23°.6	23°.1	22.38	20.63	1.00	0.67	0.34	0.02	19.27	19.35	—0.08	179.52
2.30 P.M.	23°.6	23°.7	22.42	20.63	1.00	0.67	0.34	0.02	19.27	19.35	—0.08	179.52

Displacement of manometer = 2.12 mm.

Dilution due to displacement of manometer = 0.30 per cent. Mean Mol. Wt. 179.73

H = 1 Mol. Wt. Glucose = 178.74.

Table XXI.

Original wt. normal concentration of solution, 0.9. Experiment No. 1.
Rotation of original solution, 44°.85. Manometer used, No. 13.
Rotation at conclusion of experiment, 44°.20. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.45 per cent. Cell used, A.
Calibration units of air in manometer, 434.93. Resistance of membrane, 138,000 ohms.
Time of setting up cell, 4.00 P.M., Nov. 27, 1906. Initial pressure, 16.5 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.				
Nov. 27												
10.30 P.M.	23°.8	24°.1	22.29									
Nov. 28												
10.30 A.M.	23°.9	24°.1	22.08									
2.15 P.M.	23°.9	24°.1	22.11									
5.00 "	24°.0	24°.3	22.07									
8.30 "	24°.0	24°.1	22.01									
Nov. 29												
10.00 A.M.	24°.1	23°.9	21.98									
2.00 P.M.	24°.1	23°.6	21.99									
7.00 "	24°.1	23°.6	21.91	20.16	1.01	0.65	0.31	0.02	21.55	21.81	—0.26	. .
Nov. 30												
11.00 A.M.	23°.7	22°.8	21.77	20.09	1.00	0.65	0.31	0.02	21.64	21.79	—0.15	179.90
5.00 P.M.	23°.7	23°.7	21.83	20.08	1.00	0.65	0.31	0.02	21.64	21.79	—0.15	179.90
Dec. 1												
9.30 A.M.	23°.7	23°.5	21.80	20.07	1.00	0.65	0.31	0.02	21.65	21.79	—0.14	179.82

Displacement of manometer = 2.57 mm.

Dilution due to displacement of manometer = 0.35 per cent. Mean Mol. Wt. 179.87

H = 1 Mol. Wt. Glucose = 178.74.

Table XXII.

Original wt. normal concentration of solution, 0.9. Experiment No. 2.
Rotation of original solution, 44°.85. Manometer used, No. 6.
Rotation at conclusion of experiment, 44°.4. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.00 per cent. Cell used, A.
Calibration units of air in manometer, 396.89. Resistance of membrane, 183,000.
Time of setting up cell, 4.00 P.M., Dec. 3, 1906. Initial pressure, 14.7 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Dec. 3												
8.00 P.M.	22°.3	22°.7	21.28									
Dec. 4												
10.00 A.M.	22°.4	22°.3	19.96									
2.00 P.M.	22°.5	22°.8	19.95	18.41	1.00	0.67	0.22	0.02	21.47	21.69	—0.22	180.59
5.00 "	22°.5	22°.7	19.95	18.41	1.00	0.67	0.22	0.02	21.47	21.69	—0.22	180.59
10.00 "	22°.5	23°.2	19.98	18.41	1.00	0.67	0.22	0.02	21.47	21.69	—0.22	180.59
Dec. 5												
9.00 A.M.	22°.7	22°.7	19.91	18.38	1.00	0.67	0.22	0.02	21.50	21.71	—0.21	180.47
2.00 P.M.	22°.7	23°.4	19.94	18.36	1.00	0.67	0.22	0.02	21.53	21.71	—0.18	180.21

Displacement of manometer = 0.98 mm.

Dilution due to displacement of manometer = 0.12 per cent. Mean Mol. Wt. 180.49

H = 1 Mol. Wt. Glucose = 178.74.

Table XXIII.

Original wt. normal concentration of solution, 0.9.
Rotation of original solution, 44°.85.
Rotation at conclusion of experiment, 44°.55.
Percentage loss in concentration, 0.66 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 3.45 P.M., Dec. 6, 1906.

Experiment No. 3.
Manometer used, No. 13.
Capillary depression, 0.02 atmosphere.
Cell used, A.
Resistance of membrane, 160,000 ohms.
Inital pressure, 15.8 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Dec. 6												
8.30 P.M.	22°.8	23°.9	22.46									
Dec. 7												
10.00 A.M.	23°.0	23°.3	21.65	19.94	1.00	0.65	0.14	0.02	21.63	21.73	—0.10	179.56
2.30 P.M.	23°.1	23°.3	21.69	19.98	1.00	0.65	0.14	0.02	21.58	21.74	—0.16	180.04
4.30 "	23°.1	23°.2	21.64	19.94	1.00	0.65	0.14	0.02	21.63	21.74	—0.11	179.62
Dec. 8												
12.00 M.	23°.1	22°.8	21.58	19.91	1.01	0.65	0.14	0.02	21.65	21.74	—0.09	179.46
3.00 P.M.	23°.1	23°.3	21.59	19.89	1.01	0.65	0.14	0.02	21.67	21.74	—0.07	179.30

Displacement of manometer = 1.69 mm.

Dilution due to displacement of manometer = 0.23 per cent. Mean Mol. Wt. 179.60

H = 1 Mol. Wt. Glucose 178.74.

Table XXIV.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
Rotation of original solution, 49°.4. Manometer used, No. 13.
Rotation at conclusion of experiment, 48°.95. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.91 per cent. Cell used, A.
Calibration units of air in manometer, 434.93. Resistance of membrane, 220,000 ohms.
Time of setting up cell, 11.30 A.M., Dec. 12, 1906. Initial pressure, 15 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Dec. 12												
8.45 P.M.	22°.0	22°.2	19.53									
Dec. 13												
10.00 A.M.	22°.0	21°.8	19.46									
4.45 P.M.	22°.0	22°.7	19.46	17.96	1.00	0.65	0.22	0.02	24.11	24.06	+0.05	178.38
11.00 "	22°.1	22°.2	19.44	17.97	1.00	0.65	0.22	0.02	24.09	24.07	+0.02	178.59
Dec. 14												
10.45 A.M.	22°.3	23°.0	19.44	17.92	1.01	0.65	0.22	0.02	24.16	24.09	+0.07	178.20
2.15 P.M.	22°.3	22°.6	19.45	17.96	1.01	0.65	0.22	0.02	24.11	24.09	+0.02	178.57
5.00 "	22°.3	22°.5	19.44	17.96	1.01	0.65	0.22	0.02	24.11	24.09	+0.02	178.57

Displacement of manometer = 1.49 mm.

Dilution due to displacement of manometer = 0.20 per cent. Mean Mol. Wt. 178.46

H = 1 Mol. Wt. Glucose = 178.74.

Table XXV.

Original wt. normal concentration of solution, 1.0. Experiment No. 2.
Rotation of original solution, 49°.4. Manometer used, No. 6.
Rotation at conclusion of experiment, 48°.95. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 0.91 per cent. Cell used, A.
Calibration units of air in manometer, 396.89. Resistance of membrane, 270,000 ohms.
Time of setting up cell, 12.00 M., Dec. 9, 1906. Initial pressure, 14.5 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Dec. 9												
4.30 P.M.	22°.6	22°.3	18.28									
11.30 "	22°.6	22°.1	17.86									
Dec. 10												
10.00 A.M.	22°.6	23°.5	17.90	16.48	1.01	0.67	0.22	0.02	23.98	24.11	—0.13	179.71
2.30 P.M.	22°.6	23°.3	17.88	16.47	1.00	0.67	0.22	0.02	24.00	24.11	—0.11	179.57
5.30 "	22°.6	23°.3	17.87	16.46	1.00	0.67	0.22	0.02	24.02	24.11	—0.09	179.42
Dec. 11												
10.30 A.M.	22°.7	23°.2	17.88	16.47	1.01	0.67	0.22	0.02	23.99	24.12	—0.13	179.70

Displacement of manometer = 1.56 mm.

Dilution due to displacement of manometer = 0.14 per cent. Mean Mol. Wt. 179.60

H = 1 Mol. Wt. Glucose = 178.74.

Table XXVI.

Original wt. normal concentration of solution, 1.0. Experiment No. 3.
Rotation of original solution, 49°.4. Manometer used, No. 6.
Rotation at conclusion of experiment, 48°.55. Capillary depression, 0.02 atmosphere.
Percentage loss in concentration, 1.72 per cent. Cell used, A.
Calibration units of air in manometer, 396.89. Resistance of membrane, 185,000 ohms.
Time of setting up cell, 12.30 P.M., Dec. 15, 1906. Initial pressure, 13.9 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Dilution of cell contents.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Mol. Wt. calculated from osmotic pressure.
Dec. 15												
6.00 P.M.	22°.1	22°.2	18.28									
8.15 "	22°.1	22°.1	18.07									
Dec. 16												
9.00 A.M.	22°.1	21°.9	18.00									
1.30 P.M.	22°.1	21°.8	18.03									
10.00 "	22°.1	22°.0	17.96	16.62	1.00	0.67	0.41	0.02	23.98	24.07	—0.09	179.41
Dec. 17												
10.15 A.M.	22°.1	22°.1	17.91	16.56	1.00	0.67	0.41	0.02	24.06	24.07	—0.01	178.81
12.30 P.M.	22°.1	22°.1	17.93	16.58	1.00	0.67	0.41	0.02	24.04	24.07	—0.03	178.96
5.00 "	22°.1	22°.2	17.94	16.59	1.00	0.67	0.41	0.02	24.02	24.07	—0.05	179.11

Displacement of manometer = 1.24 mm.
Dilution due to displacement of manometer = 0.17 per cent. Mean Mol. Wt. 179.07
H = 1 Mol. Wt. Glucose = 178.74.

Table XXVII.—Determination of the Osmotic Pressure of Glucose.

Series I., 1906.

Weight normal concentration.	No. of experiment.	Temperature of solution.			Osmotic pressure observed (atmospheres).			Calculated gas pressure for same temperature.			Difference between mean osmotic and mean gas pressure.	Molecular weight calculated from osmotic pressure.			Mean molecular weight for each concentration.
		Mean.	Highest.	Lowest.	Mean.	Highest.	Lowest.	Mean.	Highest.	Lowest.		Mean.	Highest.	Lowest.	
0.1	1	24°.10	24°.40	23°.90	2.39	2.39	2.38	2.42	2.43	2.42	—0.03	181.40	182.00	181.10	
"	2	25°.10	25°.20	25°.00	2.42	2.42	2.41	2.43	2.43	2.43	—0.01	179.83	180.30	179.50	180.62
0.2	1	24°.10	24°.20	24°.00	4.76	4.79	4.75	4.85	4.85	4.85	—0.09	181.77	182.30	180.70	
"	2	24°.93	25°.20	24°.70	4.77	4.78	4.76	4.86	4.86	4.86	—0.09	182.10	182.60	181.60	181.94
0.3	1	22°.20	22°.30	22°.20	7.12	7.15	7.08	7.22	7.22	7.22	—0.10	181.38	182.30	180.50	
"	2	23°.48	23°.60	23°.30	7.17	7.19	7.16	7.25	7.26	7.25	—0.08	180.73	181.10	180.30	181.06
0.4	1	26°.90	27°.00	26°.80	9.70	9.72	9.67	9.78	9.79	9.78	—0.08	180.21	180.80	179.83	
"	2	26°.60	26°.70	26°.60	9.65	9.67	9.63	9.77	9.78	9.77	—0.12	181.02	181.49	180.69	180.62
0.5	1	21°.86	21°.90	21°.75	12.07	12.09	12.05	12.03	12.03	12.02	+0.04	178.12	178.31	177.81	
"	2	24°.17	24°.50	23°.80	12.00	12.02	11.98	12.12	12.13	12.10	—0.12	180.57	180.87	180.24	179.35
0.6	1	22°.57	22°.70	23°.30	14.56	14.62	14.47	14.46	14.47	14.43	+0.10	177.62	178.52	176.95	
"	2	22°.40	22°.45	22°.35	14.32	14.36	14.31	14.40	14.40	14.39	—0.08	180.42	180.60	179 92	
"	3	22°.30	22°.40	22°.30	14.29	14.32	14.26	14.45	14.46	14.45	—0.16	180.83	181.21	180.39	179.62
0.7	1	22°.26	22°.32	22°.20	16.82	16.82	16.81	16.85	16.86	16.85	—0.03	179.18	179.28	179.11	
"	2	25°.43	25°.60	25°.30	16.96	17.06	16.87	17.04	17.05	17.03	—0.08	179.55	180.61	178.45	
"	3	22°.70	22°.70	22°.70	16.75	16.76	16.74	16.88	16.88	16.88	—0.13	180.16	180.27	180.06	179.63
0.8	1	23°.00	23°.00	23°.00	19.27	19.28	19.26	19.31	19.31	19.31	—0.04	179.16	179.25	179.06	
"	2	23°.28	23°.50	23°.10	19.16	19.19	19.13	19.33	19.35	19.32	—0.17	180.39	180.53	180.21	
"	3	23°.64	23°.70	23°.60	19.25	19.27	19.22	19.35	19.36	19.35	—0.10	179.73	180.05	179.52	179.76
0.9	1	23°.80	24°.10	23°.70	21.64	21.65	21.64	21.80	21.81	21.79	—0.16	179.87	179.90	179.82	
"	2	22°.58	22°.70	22°.50	21.49	21.53	21.47	21.70	21.71	21.69	—0.21	180.49	180.59	180.21	
"	3	23°.10	23°.10	23°.00	21.63	21.67	21.58	21.74	21.74	21.73	—0.11	179.60	180.04	179.30	179.99
1.0	1	22°.20	22°.30	22°.00	24.12	24.16	24.09	24.08	24.09	24.06	+0.04	178.46	178.59	178.20	
"	2	22°.60	22°.70	22°.60	24.00	24.02	23.98	24.11	24.12	24.11	—0.11	179.60	179.71	179.42	
"	3	22°.10	22°.10	22°.10	24.03	24.06	23.98	24.07	24.07	24.07	—0.04	179.07	179.41	178.81	179.04

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 180.08

Table XXVIII.—Determination of the Osmotic Pressure of Glucose.

Series I., 1906. Summary of Results.

Weight normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Difference between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration
0.1	1	24°.10	2.39	2.42	—0.03	181.40	
"	2	25°.10	2.42	2.43	—0.01	179.83	180.62
0.2	1	24°.10	4.76	4.85	—0.09	181.77	
"	2	24°.93	4.77	4.86	—0.09	182.10	181.94
0.3	1	22°.20	7.12	7.22	—0.10	181.38	
"	2	23°.48	7.17	7.25	—0.08	180.73	181.06
0.4	1	26°.90	9.70	9.78	—0.08	180.21	
"	2	26°.60	9.65	9.77	—0.12	181.02	180.62
0.5	1	21°.86	12.07	12.03	+0.04	178.12	
"	2	24°.17	12.00	12.12	—0.12	180.57	179.35
0.6	1	22°.57	14.56	14.46	+0.10	177.62	
"	2	22°.40	14.32	14.40	—0.08	180.42	
"	3	22°.30	14.29	14.45	—0.16	180.83	179.62
0.7	1	22°.26	16.82	16.85	—0.03	179.18	
"	2	25°.43	16.96	17.04	—0.08	179.55	
"	3	22°.70	16.75	16.88	—0.13	180.16	179.63
0.8	1	23°.00	19.27	19.31	—0.04	179.16	
"	2	23°.28	19.16	19.33	—0.17	180.39	
"	3	23°.64	19.25	19.35	—0.10	179.73	179.76
0.9	1	23°.80	21.64	21.80	—0.16	179.87	
"	2	22°.58	21.49	21.70	—0.21	180.49	
"	3	23°.10	21.63	21.74	—0.11	179.60	179.99
1.0	1	22°.20	24.12	24.08	+0.04	178.46	
"	2	22°.60	24.00	24.11	—0.11	179.60	
"	3	22°.10	24.03	24.07	—0.04	179.07	179.04

H = 1 Mol. Wt. Glucose = 178.74 Mean Mol. Wt. 180.08

give for cane sugar[1] the information which is embodied for glucose in Table XXVIII.

Finally, in Table XXXI., all the results which have been obtained up to the present time, at temperatures between 18° and 26°, both for cane sugar and for glucose, are brought together in the from of ratios of osmotic to calculated gas pressure at the same temperatures.

[1] THIS JOURNAL, 34, 1; 36, 39.

Table XXIX.—Determination of the Osmotic Pressure of Cane Sugar.

Series I., 1905. Summary of Results.

Weight normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Differences between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration
0.1	1	18°.85	2.43	2.38	+0.05	334.47	
"	2	18°.71	2.42	2.38	+0.05	334.08	334.28
0.2	1	20°.59	4.73	4.79	—0.06	344.50	
"	2	20°.91	4.79	4.80	—0.01	340.03	342.27
0.25	1	23°.45	6.08	6.05	+0.03	338.05	
"	2	21°.46	5.94	6.02	—0.08	344.60	341.33
0.3	1	19°.28	7.18	7.17	+0.01	339.44	
"	2	17°.65	7.18	7.13	+0.05	337.65	338.55
0.4	1	18°.88	9.45	9.55	—0.10	343.21	
"	2	20°.94	9.65	9.61	+0.04	338.54	340.88
0.5	1	20°.84	11.93	12.01	—0.08	341.92	
"	2	20°.32	12.06	11.99	+0.07	337.85	339.89
0.6	1	21°.38	14.22	14.45	—0.23	345.09	
"	2	24°.45	14.37	14.59	—0.22	344.89	344.99
0.7	1	20°.14	16.66	16.77	—0.11	342.18	
"	2	24°.62	16.89	17.03	—0.14	342.41	342.30
0.8	1	17°.89	19.20	19.03	+0.17	336.46	
"	2	19°.56	19.35	19.13	+0.22	335.86	336.16
0.89101	1	19°.34	21.03	21.30	—0.27	343.90	343.90
0.9	1	19°.84	21.68	21.55	+0.13	337.55	337.55
1.0	1	23°.32	24.56	24.26	+0.30	335.50	
"	2	22°.44	24.28	24.15	+0.13	337.95	
"	3	21°.60	24.17	24.09	+0.08	338.54	337.33

H = 1. Final mean of Mol. Wts., 339.95

Theoretical Mol. Wt., 339.60

It is clear, as it was in the case of cane sugar,[1] that *glucose in aqueous solution, at temperatures in the vicinity of 20°, exerts an osmotic pressure equal to that which a molecular-equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to that of the solvent in the pure state.* This rule holds equally well throughout all the concentrations whose pressure we have measured, and the deviations from it do not exceed the known but unavoidable experimental errors of the work.

[1] THIS JOURNAL, 34, 93; 36, 87.

Table XXX.—Determination of the Osmotic Pressure of Cane Sugar.

Series II., 1906. Summary of Results.

Weight normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Difference between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration
0.1	1	24°.06	2.51	2.42	+0.09	327.85	
"	2	24°.23	2.55	2.43	+0.12	322.56	325.21
0.2	1	20°.90	4.72	4.79	—0.07	344.96	
"	2	21°.38	4.78	4.80	—0.02	344.90	
"	3	21°.77	4.81	4.81	0.00	339.74	341.87
0.3	1	21°.67	7.24	7.21	+0.03	338.37	
"	2	19°.88	7.20	7.16	+0.04	338.20	338.29
0.4	1	21°.63	9.64	9.61	+0.03	338.73	
"	2	22°.15	9.69	9.63	+0.06	337.50	338.12
0.5	1	22°.62	12.06	12.06	0.00	339.59	
"	2	23°.70	12.23	12.10	+0.13	336.19	337.89
0.6	1	24°.38	14.74	14.55	+0.19	335.32	
"	2	24°.24	14.70	14.55	+0.15	336.07	
"	3	24°.10	14.77	14.54	+0.23	334.32	335.24
0.7	1	23°.64	16.95	16.94	+0.01	339.39	
"	2	23°.90	16.96	16.93	+0.03	339.50	339.45
0.8	1	23°.60	19.30	19.35	—0.05	340.48	
"	2	23°.69	19.39	19.36	+0.03	339.08	339.78
0.9	1	24°.79	21.82	21.86	—0.04	340.19	
"	2	24°.76	21.91	21.86	+0.05	338.82	339.51
1.0	1	23°.56	24.42	24.19	+0.23	336.39	
"	2	24°.58	23.98	24.28	—0.30	342.72	339.56

H = 1 Final mean of Mol. Wts., 337.49

Theoretical Mol. Wt., 339.60

In papers soon to follow this, it will be shown that at temperatures near the freezing point of the solvent, neither cane sugar nor glucose obeys the rule formulated above, that both substances, in the neighborhood of 0°, exert pressures somewhat in excess of the calculated gas pressures.

A second and important conclusion which is to be drawn from the results is that, at the temperatures at which the measurements were made (*i. e.*, between 18° and 26°, in round numbers), both cane sugar and glucose in solution are in the

Table XXXI.—Ratio of Observed Osmotic to Calculated Gas Pressure at the Same Temperature, the Volume of the Gas Being That of the Solvent in the Pure State.

Weight normal concentration.	No. of experiment.	Cane Sugar. Series I. Temperature.	Series I. Ratio.	Series II. Temperature.	Series II. Ratio.	Glucose. Series I. Temperature.	Series I. Ratio.
0.1	1	18°.85	1.021	24°.06	1.037	24°.10	0.988
"	2	18°.71	1.017	24°.23	1.049	25°.10	0.996
0.2	1	20°.59	0.987	20°.90	0.985	24°.10	0.981
"	2	20°.91	0.998	21°.38	0.996	24°.93	0.981
"	3			21°.77	1.000		
0.25	1	23°.45	1.005				
"	2	21°.46	0.987				
0.3	1	19°.28	1.001	21°.67	1.004	22°.20	0.986
"	2	17°.65	1.007	19°.88	1.006	23°.48	0.989
0.4	1	18°.81	0.990	21°.63	1.003	26°.90	0.992
"	2	20°.94	1.004	22°.15	1.006	26°.60	0.988
0.5	1	20°.84	0.993	22°.62	1.000	21°.86	1.003
"	2	20°.32	1.006	23°.70	1.010	24°.17	0.990
0.6	1	21°.38	0.984	24°.38	1.013	22°.57	1.007
"	2	24°.45	0.984	24°.70	1.010	22°.46	0.994
"	3			24°.10	1.016	22°.30	0.988
0.7	1	20°.14	0.993	23°.64	1.000	22°.26	0.998
"	2	24°.62	0.992	23°.90	1.002	25°.43	0.995
"	3					22°.70	0.992
0.8	1	17°.89	1.009	23°.60	0.997	23°.00	0.998
"	2	19°.56	1.012	23°.69	1.002	23°.28	0.991
"	3					23°.64	0.995
0.89101	1	19°.34	0.987				
0.9	1	19°.84	1.006	24°.79	0.998	23°.80	0.993
"	2			24°.76	1.002	22°.58	0.990
"	3					23°.10	0.995
1.0	1	23°.32	1.012	23°.56	1.010	22°.20	1.002
"	2	22°.44	1.005	24°.58	0.988	22°.60	0.995
"	3	21°.60	1.003			22°.10	0.998

anhydrous condition; for it requires only a very elementary course of reasoning to show that, if solutions made up, as ours are, with a fixed mass of the solvent, exhibit an osmotic pressure strictly proportional to their supposed concentration, the dissolved material cannot have appropriated any portion of the solvent. The only alternative, apparently, is the proposition that the absolute amount of water abstracted from the

solvent is the same for all solutions, *i. e.*, wholly independent of concentration.

The Depression of the Freezing Points of Glucose Solutions.

The following table (XXXII.) gives for each weight-normal concentration of our glucose solutions (1) the observed depression of the freezing point, (2) the molecular lowering of the freezing point, (3) the density at 0°. The thermometer which was used in this part of the work has been described in connection with similar data for cane sugar.[1] It had been tested at the "*Reichsanstalt*," and further corrections were made for the subsequent shrinkage of the bulb.

Table XXXII.

Weight normal concentration.	Observed depression of the freezing point.	Molecular lowering of the freezing point.	Density of the solution at 0°.
0.1	0°.192	1.92	1.00687
0.2	0°.386	1.92	1.01376
0.3	0°.576	1.92	1.02041
0.4	0°.762	1.91	1.02691
0.5	0°.952	1.91	1.03327
0.6	1°.147	1.91	1.03945
0.7	1°.337	1.91	1.04551
0.8	1°.528	1.91	1.05143
0.9	1°.720	1.91	1.05731
1.0	1°.918	1.92	1.06300

The notable feature of the data presented in the table is the proportionality of the freezing point depressions to the weights of glucose dissolved in the fixed quantity of water, which relation, like the similar one between osmotic pressure and concentration, at higher temperatures, may be interpreted as indicating that glucose does not, even at the freezing temperatures of its aqueous solutions, appropriate any portion of the solvent. The bearing of this relation upon the question of hydration in solution will be brought forward again in connection with the osmotic pressures which glucose and cane sugar solutions have been found to exert in the vicinity of 0°.

JOHNS HOPKINS UNIVERSITY,
December 24, 1906.

[1] THIS JOURNAL, 36, 89.

ON SOME SEMICARBAZIDE DERIVATIVES OF ISOPROPIONIC ACID, BENZOIC ACID AND BENZENESULPHONIC ACID.

By S. F. Acree.

(NINTH COMMUNICATION ON THE URAZOLES.)

[The writer is indebted to the Carnegie Institution, of Washington, for aid in this work.]

In order to pursue some of the physical chemical problems connected with the semicarbazides and urazoles,[1] now being studied in this laboratory, it became necessary to attempt to prepare a number of these substances having greater solubilities in water and in alcohol than do most phenylsemicarbazide and phenylurazole derivatives.

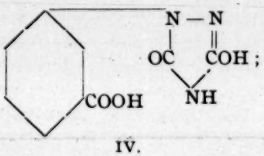
Especially is it desirable to investigate a large number of semicarbazide derivatives of fatty and aromatic acids, such as the following:

I. $NH_2CONHNHCH(CH_3)COOH$;

II. $NH_2CONHNHC_6H_4COOH$;

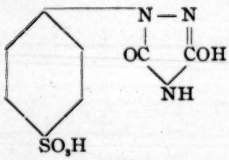
III. $NH_2CONHNHC_6H_4SO_3H$;

and also a number of corresponding triazole and urazole derivatives, such as

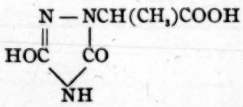


IV.

[1] This Journal, 27, 118; 31, 185; 32, 606; 37, 71. Ber. d. chem. Ges., 38, 553; 36, 3139; 37, 184, 618.

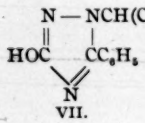


V.

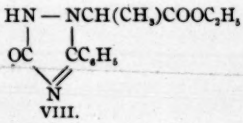


VI.

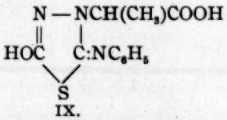
The writer, in conjunction with J. R. Bailey,[1] prepared a number of 1-*iso*propionic acid 3-oxy-5-alkyltriazoles, and their corresponding esters and salts, and also some derivatives of 1,5-dihydro-3-oxy-5-phenylimido-4,1,2-thiodiazole-1-propionic acid (IX.). The ethyl 3-oxy-5-phenyl-1-isopropionate occurs in two modifications, one of which seems to be an enol form, VII., and the other a keto form, VIII.



VII.



VIII.



IX.

All these substances, with an acid side chain, have proved to be more soluble in water than phenylurazole, and physical chemical investigations are being made on them and their derivatives. The influence of the acids in the side group on the amide groups of the urazole and triazole rings, and the simultaneous change in tautomeric relationships, will be made special subjects of investigation. The corresponding thiosemicarbazides, thiourazoles and thiotriazoles will be made and studied in this connection, and various phenylurazoles with basic groups attached to the benzene ring will be investigated from the same standpoints.

[1] Ber. d. chem. Ges., **33**, 1520; J. Am. Chem. Soc., **26**, 1016.

p-Hydrazinobenzenesulphonic Acid, $H_2NNHC_6H_4SO_3H$.—This substance was prepared according to the following modification of Richter's method:[1] Thirty grams of phenylhydrazine were added to 180 grams of concentrated sulphuric acid; the white precipitate of the salt redissolved when the mixture was stirred and heated. The solution was heated 15 minutes at 100°, and it then began to foam. The mixture was poured into 200 cc. of water and stirred well and cooled, whereupon a pinkish precipitate of *p*-hydrazinebenzenesulphonic acid was formed. This was filtered and dissolved in the necessary amount of 10 per cent sodium hydroxide solution, filtered, and an excess of sodium hydroxide was added. A heavy precipitate of the sodium salt was formed, which is not very soluble in cold water, but readily soluble in hot water. When a solution of this sodium salt was made acid the *p*-hydrazinebenzenesulphonic acid precipitated out pure.

The sodium salt is white. A solution of silver nitrate, when added to one of the sodium salt, is reduced instantly. Analysis:

1.1950 gram sodium salt lost 0.1685 gram H_2O when heated three hours at 140°.

0.1930 gram crystallized salt required 6.84 cc. of 1.125 0.1 N HCl (methyl orange).

	Calculated for $C_6H_7N_2SO_3Na.2H_2O$.	Found.
H_2O	14.62	14.10
Na	9.36	9.19

α-Semicarbazido-p-Benzenesulphonic Acid, $NH_2CONHNHC_6H_4SO_3H$.—When 5 grams of *p*-hydrazinobenzenesulphonic acid were warmed with a solution of one molecular proportion of potassium cyanate in a small amount of water, all of the acid dissolved. When the solution was cooled, crystals of the potassium salt began to appear and when alcohol was added 5.75 grams of pure white potassium semicarbazido-*p*-benzenesulphonate precipitated out. When

[1] Ber. d. chem. Ges., 18, 3172. Cf. Claisen and Roosen Ann. Chem. (Liebig), 278, 297.

a concentrated solution of some of this salt was treated with an excess of concentrated hydrochloric acid, a precipitate of the semicarbazido-*p*-benzenesulphonic acid was formed. This melts at 243°, is very soluble in water and colors methyl orange red. Titration:

0.2339 gram acid required 10.06 cc. 0.1 N sodium hydroxide solution (phenolphthalein); calculated, 10.11 cc.

The potassium salt seems to contain no water of crystallization. When 1.0417 grams of salt were heated at 140°, during 5 hours, it lost 0.0062 gram of water. When 0.2568 gram of salt was heated at 140°, during 2 hours, it lost 0.0037 gram of water. When a solution of the salt is treated with a solution of silver nitrate no precipitate is formed, but a mirror of silver is deposited on the vessel slowly in the cold and immediately on heating. The salt decolorizes cold potassium permanganate solutions at once, and manganese dioxide is precipitated. Solutions of the salt give no precipitates with barium chloride, lead nitrate, calcium chloride, cobalt nitrate, ferric chloride, copper sulphate (the solution turns pink), mercuric chlorde and mercurous nitrate. Analysis:

0.3971 gram salt, dried at 110°, gave 0.1232 gram K_2SO_4.

0.1527 gram salt, dried at 110°, gave 25 cc. N at 19° (24.2 cc. at 12°) and 627 mm.

	Calculated for $C_7H_8N_3O_4SK$.	Found.
N	15.64	15.51
K	14.53	13.92

α-Carbethoxysemicarbazido-α-isopropionic Nitrile, $NH_2CONHN(COOC_2H_5)CH(CH_3)CN$.—To prepare the α-semicarbazidoisopropionic nitrile,[1] 50 grams of semicarbazide hydrochloride and 29 grams of pure acetic aldehyde ammonia were ground together very intimately for 1 hour. The mixture was put into 250 cc. of pure hydrocyanic acid and allowed to stand 8 days, with frequent agitation. The prussic acid had been slowly distilled twice through a long upward condenser and a second downward condenser connected with the first. Water having a temperature of 27°–28° was run through the

[1] Bailey and Acree: Ber. d. chem. Ges., 33, 1524, 1531, 1532.

first condenser, whereas cold tap water was run through the second condenser. After the reaction was at an end the prussic acid was distilled off, the last portion being removed by a current of air. The residue was extracted with absolute ethyl alcohol in order to dissolve the nitrile and leave the ammonium chloride. The alcoholic extracts gave, upon evaporation, nearly a quantitative yield of α-semicarbazidoisopropionic nitrile, which melted at 124°.

Three grams of the nitrile were boiled 6 hours, in benzene solution, with 3 grams of ethyl chlorcarbonate in a flask under a return condenser; an oil separated out at the bottom. The benzene was evaporated off and the residue was dissolved in a mixture of alcohol and benzene; when the solvent was allowed to evaporate spontaneously, crystals of the pure α-carbethoxysemicarbazido-α-isopropionic nitrile were formed, which, after crystallizaion from alcohol, melted at 173°. The substance is very soluble in acetone, fairly soluble in ethyl acetate, water and alcohol, and difficultly soluble in chloroform.

The substance was treated with a molecular proportion of barium hydroxide in cold solution to saponify the nitrile and ester groups. The resulting solution was acidified and only by evaporation was the resulting urazole-α-isopropionic acid obtained. This is now under investigation. Analysis:

0.1084 gram substance gave 31.8 cc. N at 16° and 625 mm.

	Calculated for $C_7H_{12}N_4O_3$.	Found.
N	28.06	28.09

o-Hydrazinobenzoic Acid, $NH_2NHC_6H_4COOH$.—This compound was made according to Fisher's method.[1] By diazotizing anthranilic acid and reducing the diazo compound with zinc and acetic acid till the solution is colorless, filtering and then adding hydrochloric acid, a precipitate is formed which is a mixture of the hydrochlorides of anthranilic acid and orthohydrazinobenzoic acid. A sample of the orthohydrazinobenzoic acid hydrochloride was made for us by Kahlbaum and is now listed by him. The sample furnished was found to con-

[1] Ber. d. chem. Ges., 13, 680.

sist of about 60 per cent anthranilic acid hydrochloride and 40 per cent *o*-hydrazinobenzoic acid hydrochloride. When the mixture of these hydrochlorides was dissolved in a small quantity of water and treated with a saturated solution of a little more than a molecular quantity of sodium acetate, a precipitate was formed at once which the analyses show to be a mixture of the free bases. When this is crystallized twice from alcohol the pure *o*-hydrazinobenzoic acid is obtained. This is sparingly soluble in cold alcohol and in ether, whereas the anthranilic acid is readily soluble in these two liquids. The pure *o*-hydrazinobenzoic acid forms both basic and acid salts. It melts at 249°, probably going over into the anhydride below this temperature. Titration and analyses:

0.1015 gram impure *o*-hydrazinobenzoic acid required 6.87 cc. 0.0994 N potassium hydroxide solution; calculated, 6.71 cc.

I. 0.1147 gram Kahlbaum substance, m. p. 243°, gave 15.15 cc. N, measured over 30 per cent potassium hydroxide at 20° and 772.7 mm.

II. 0.1139 gram Kahlbaum substance, m. p. 243°, gave 15.2 cc. N, measured over 30 per cent potassium hydroxide at 20° and 771.7 mm.

III. 0.1176 gram pure substance, m. p. 249°, gave 19.3 cc. N, measured over 30 per cent potassium hydroxide at 23° and 756.7 mm.

	Calculated for $C_7H_8N_2O_2$.	Calculated for $C_7H_7NO_2$.	Found. I.	II.	III.
N	18.46	10.24	15.23	15.54	18.52

o-Hydrazinobenzoic Acid Hydrochloride.[1]—The sample furnished by Kahlbaum melted at 207° and was mixed with a considerable quantity of a colored substance insoluble in water. The hydrochloride is very soluble in alcohol and in water and when pure is white. Titration and analyses:

0.1000 gram substance required 11.35 cc. 0.907 0.1 N potassium hydroxide solution; calculated, 11.59 cc.

I. 0.1100 gram substance gave 15.5 cc. N, measured over 30 per cent potassium hydroxide solution, at 29°.5 and 759.3 mm.

[1] **Emil Fischer**: *loc. cit.*

II. 0.1115 gram substance gave 15.2 cc. N, measured over 30 per cent potassium hydroxide solution, at 24°.8 and 762 mm.

	Calculated for $C_7H_8N_2O_2Cl$.	Found. I.	II.
N	14.92	15.44	15.35

o-Hydrazinobenzoic Acid Hydrobromide.—A sample of the pure hydrazinobenzoic acid was treated with a slight excess of hydrobromic acid solution and evaporated in a desiccator. Needles of the hydrobromide were formed, which melted at 207°–210°. This salt is apparently more soluble in water than the hydrochloride. Titration:

0.1412 gram hydrobromide required 12.25 cc. 0.0994 N potassium hydroxide solution; calculated, 12.25 cc.

α-Semicarbazidoorthobenzoic Acid, $NH_2CONHNHC_6H_4COOH$.—Ten grams of orthohydrazinobenzoic acid hydrochloride were treated with 8 cc. of 33 per cent potassium hydroxide solution and 5 grams of potassium cyanate in 25 cc. of water and the mixture was shaken until the hydrochloride was completely dissolved. The resulting solution was acidified with acetic acid and the α-semicarbazidoorthobenzoic acid precipitated nearly completely. The yield was 8.5 grams. The semicarbazide derivative was also formed when the *o*-hydrazinobenzoic acid hydrochloride was shaken with 2 molecules of potassium cyanate in water until the hydrochloride dissolved completely; the substance precipitated out when sulphuric acid was added. The semicarbazide derivative melts at 225°, is somewhat soluble in water, and is very soluble in alcohol. It titrates against alkali as a monobasic acid, and is reprecipitated unchanged from these solutions when strong acids are added.

A solution of the potassium salt was treated with the molecular amount of silver nitrate in solution. A white silver salt precipitated out, but turned black very soon. A solution of 0.5 gram of the acid, in a slight excess of alkali, was treated with the theoretical amount of 0.1 N potassium permanganate solution. The permanganate solution was decolorized in-

stantly; the manganese dioxide was filtered off and the solution of the azo compound was evaporated to a small volume. When sulphuric acid was added, a precipitate of a red sub stance, which is probably the *o*-benzoic acid azocarbamide, $NH_2CON : NC_6H_4COOH$, was formed. This was very hygroscopic and was not analyzed. Titration and analysis:

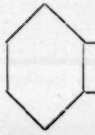
0.1000 gram substance required 5.14 cc. 0.1 N potassium hydroxide solution (phenolphthalein); calculated, 5.13 cc.

0.1825 gram substance gave 33.4 cc. N at 18° and 750 mm.

	Calculated for $C_8H_9N_3O_3$.	Found.
N	21.52	20.82

Potassium δ-Phenylthiosemicarbazido-α-orthobenzoate, $C_6H_4(COOK)NHNHCSNHC_6H_5$.—This compound was made by shaking potassium *o*-hydrazinobenzoate in dilute alcohol, with the equivalent quantity of phenyl mustard oil until the odor of the latter disappeared. When the solution was evaporated to dryness the salt was obtained.

δ-Phenylthiosemicarbazido-α-orthobenzoic Anhydride,



.—When the potassium salt above described was treated with dilute sulphuric acid a precipitate was formed. This was crystallized from alcohol; it then melted at 238°. The substance was neutral and was not changed when evaporated with alkaline solutions, or with lead oxide. Hence the substance must have the sulphur atom in the ring as represented in the formula; any other formula would be that of a substance necessarily soluble in alkalies.

This shows that the α-orthobenzoic acid δ-phenylthiosemicarbazide does not exist except in the form of salts. It loses a molecule of water and forms an anhydride just as

1-phenyl-1-carboxylic acid semicarbazide[1] spontaneously loses a molecule of water and forms phenylurazole. Analysis:

0.1562 gram substance gave 21.6 cc. N at 21° and 754.6 mm.

	Calculated for $C_{14}H_{11}ON_3S$.	Found.
N	15.64	15.60

JOHNS HOPKINS UNIVERSITY,
January 1, 1907.

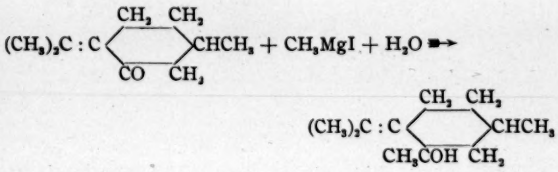
THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

XI. CYCLIC KETONES.

BY E. P. KOHLER.

The experiments described in this paper were performed with the 3 best known types of unsaturated ring ketones, namely: Those which contain unsaturated side chains, those which have an unsaturated nucleus, and those which have 2 ethylene linkages, one of which is in the nucleus, the other in the side chain.

Only one experiment with a ketone of the first type has been described. Grignard[2] added pulegone to methylmagnesium iodide and obtained a hydrocarbon, evidently formed by loss of water from an intermediate tertiary alcohol.

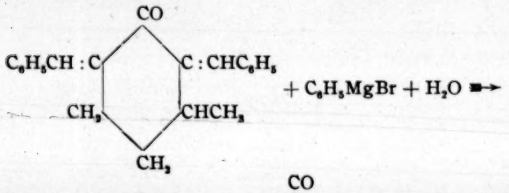


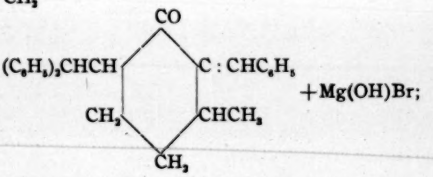
The reaction in this case involved only the carbonyl group but since unsaturated cyclic ketones of this type generally

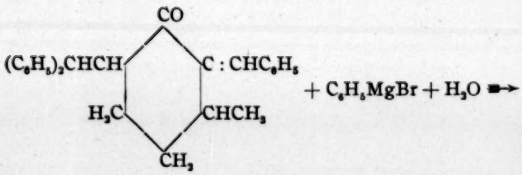
[1] Acree: Ber. d. chem. Ges., 37, 618. Cf. Bailey and Acree: J. Am. Chem. Soc. 26, 1012.

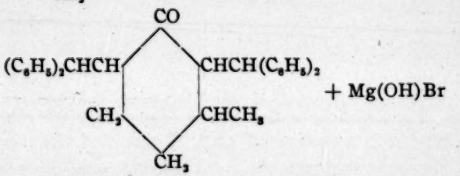
[2] Ann. Chim. Phys. [7], 24, 483.

behave like the corresponding open-chain compounds, it seemed probable that this result was due to the presence of the 2 methyl groups in combination with one of the unsaturated carbon atoms. The behavior of dibenzalcyclomethylhexanone confirmed this view. This ketone reacts exactly like dibenzalacetone and gives, ultimately, a mixture of stereoisomeric saturated ketones:





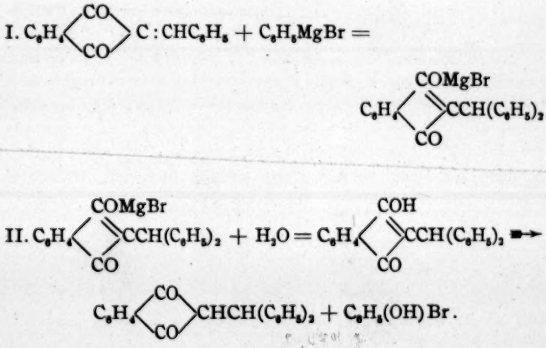




It was possible to prove that these ketones are formed by

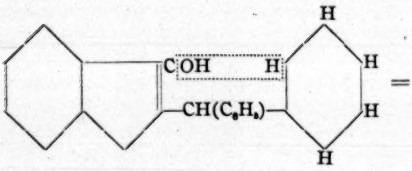
1,4-addition. In the last paper[1] it was shown that enols which are formed by 1,4-addition to open-chained unsaturated ketones which have a hydrocarbon residue in the *a*-position are sufficiently stable to permit of transformation into peroxides. This rule appears to hold for the enols obtained from the first type of cyclic ketones. Thus the products obtained from dibenzalcyclomethylhexanone, which is essentially an *a,a*-disubstitution product of dibenzalacetone, were readily transformed into peroxides, while no peroxides could be obtained in experiments with dibenzalacetone.

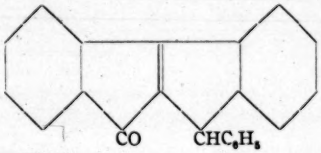
An interesting result was obtained with benzaldiketohydrindene. The reactions to be expected with this substance are represented by the following equations:



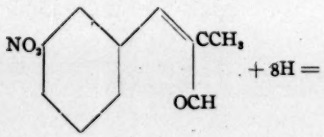
The product, however, does not have the composition of the saturated diketone represented, differing from it by 1 molecule of water. Its properties indicate that a new indene ring has been formed, the enol losing water instead of undergoing the usual rearrangement to ketone:

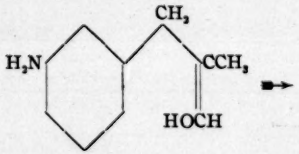
[1] THIS JOURNAL, 36, 529.



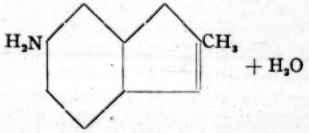


It is probable that a similar process accounts for the peculiarities that have been observed in the formation of simpler indene derivatives from unsaturated compounds. Miller and Rohde[1] found that, while no indene derivative can be obtained by reducing either α-methylcinnamic aldehyde or *m*-nitrocinnamic aldehyde, *m*-nitro-α-methylcinnamic aldehyde is readily reduced to 2-methyl-6-aminoindene. It is easy to account for these results if we assume that the reduction consists in 1,4-addition of hydrogen:



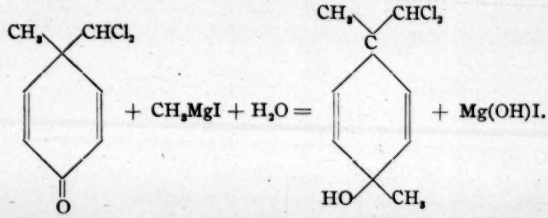


[1] Ber. d. chem. Ges., 22, 1830.



The amino group increases the reactivity of the hydrogen atom in the para position and the methyl group is necessary to impart sufficient stability to the enol[1] and prevent immediate rearrangement to saturated aldehyde.

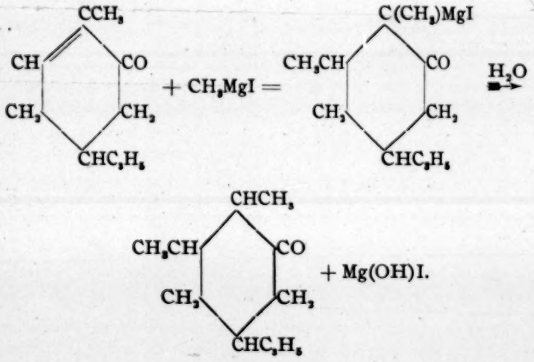
The reaction between Grignard's reagent and ketones of the second type was first studied by Bamberger and Blangley,[2] who found that toluquinone and xyloquinone give quinoles by addition to the carbonyl group. A little later Auwers and his assistants[3] published results obtained in a very thorough investigation of the reaction with unsaturated cyclic ketones obtained by condensing chloroform with phenols. These also form only 1,2-addition products.



It is clear, from these results, that 1,4-addition products with Grignard's reagent are not obtained with the simplest ketones of this type; but whether a different result would be obtained with ketones in which the reactivity of the carbonyl group is diminished by substituents in the α-position remained to be determined. The most promising substance for this purpose seemed to be carvone. It is easily obtained in any

[1] THIS JOURNAL, **36**, 529.
[2] Ber. d. chem. Ges., **36**, 1625.
[3] *Ibid.*, **36**, 1861.

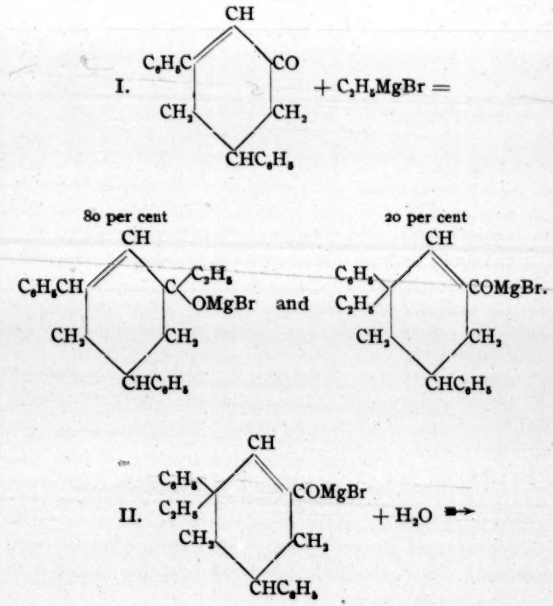
desired quantity, it readily enters into addition reactions that involve the ethylene linkage in the nucleus,[1] and since the substituent in the α-position is a hydrocarbon residue, it was probable that any 1,4-addition that might take place could be recognized by the peroxide reaction. The experiments with carvone were barely finished when papers on the same subject were published by Rupe and Liechtenhan[2] and by Klages and Sommer.[3] My results confirm those published by Rupe and Liechtenhan. When the ketone is added to Grignard's reagent at low temperatures, about 75 per cent of the product is a tertiary alcohol or a hydrocarbon formed from this alcohol and the remainder a new ketone. Rupe and Liechtenhan assume that the ketone is formed by 1,2-addition to the ethylene linkage:

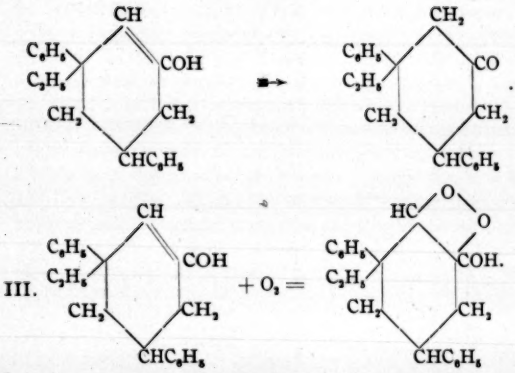


This assumption is certainly wrong. Ketones obtained by the action of Grignard's reagent on unsaturated cyclic ketones are due to 1,4-addition. It is difficult to prove this satisfactorily with carvone, because it is impossible to separate the sensitive substances required for this purpose from the

[1] Ber. d. chem. Ges., **37**, 4465.
[2] *Ibid.*, **39**, 1119.
[3] *Ibid.*, **39**, 2306.

large quantity of indifferent, high-boiling liquids formed at the same time. In the case of diphenylcyclohexanone, however, which gives solid products, the proof is conclusive. This ketone reacts with ethylmagnesium bromide exactly like carvone. If the product is isolated in the usual way, about 80 per cent of it is an unsaturated tertiary alcohol, or a hydrocarbon formed from the alcohol by loss of water—the remainder is a saturated ketone. But if the magnesium derivative is decomposed with sufficient care and the ether evaporated in a current of oxygen, the result is a mixture of tertiary alcohol and enolic peroxide:





III.

It has been pointed out that in open-chained compounds the direction of the reaction sometimes depends upon the magnesium compound that is used. The same is true in the case of diphenylcyclohexanone. With phenylmagnesium bromide the sole product is a tertiary alcohol, formed by 1,2-addition to carbonyl, while with ethylmagnesium bromide the product is a mixture of tertiary alcohol with ketone formed by 1,4-addition. Diphenylcyclohexanone also forms complex products like those obtained from open-chained unsaturated compounds when the organic magnesium compound is not present in sufficient excess. All the results obtained with this type of unsaturated ketone indicate that there is no qualitative difference between their behavior towards Grignard's reagent and that of open-chained unsaturated compounds.

EXPERIMENTAL PART.

Experiments with Dibenzalcyclomethylhexanone.

The ketone used in these experiments was made by introducing 2 benzal groups[1] into methylhexanone obtained from pulegone. When the finely powdered substance is added to

[1] Ber. d. chem. Ges., 39, 1597.

excess of ethereal phenylmagnesium bromide it reacts like open-chained unsaturated ketones; the bright red intermediate compound that first forms readily redissolves and the reaction is complete as soon as all the color has disappeared. The product, isolated in the usual way, is a mixture that can be separated by repeated crystallization from chloroform and absolute alcohol. The least soluble substance obtained crystallizes from chloroform in hard needles, melting at 192°. It is readily soluble in chloroform and benzene, moderately in acetone and ethyl acetate, sparingly in boiling absolute alcohol and ether. A more soluble product accumulated in the mother liquors. This separated from absolute alcohol in long, fine needles melting at 132°. It is readily soluble in chloroform, acetone and absolute alcohol. The combined filtrates from these compounds slowly deposited long needles, melting at 154°–156°, but this third product was not obtained in sufficient quantity for analysis:

I. 0.1337 gram substance (192°) gave 0.4340 gram CO_2 and 0.0866 gram H_2O.

II. 0.1604 gram substance (132°) gave 0.5200 gram CO_2 and 0.1071 gram H_2O.

	Calculated for $C_{27}H_{26}O$.	Found. I.	II.
C	88.52	88.50	88.32
H	7.10	7.11	7.21

Both of these substances dissolve in concentrated sulphuric acid and give orange-colored solutions; both decolorize a solution of bromine in chloroform and reduce potassium permanganate dissolved in acetone. The analytical results show that the substances are isomeric and the behavior towards phenylmagnesium bromide described below proves that they are ketones. As the original ketone is unsymmetrical and the product contains 2 asymmetric carbon atoms, both structural and spatial isomerism is possible, and the location of the benzal and diphenylmethyl groups is uncertain.

Peroxides.—When a rapid current of oxygen was passed through the ethereal solution obtained by decomposing the magnesium derivatives from dibenzalmethylcyclohexanone,

with iced hydrochloric acid, the result was a mixture of peroxides quite free from ketones. It was extremely difficult to get a pure substance from this mixture of sensitive compounds. The best results were obtained by solution in chloroform, followed by very slow precipitation with ligroin. After many repetitions of this operation two compounds melting at 176° and 142° were finally obtained in quantities sufficient for analysis. Both substances crystallized in colorless needles and decomposed a few degrees above the melting point.

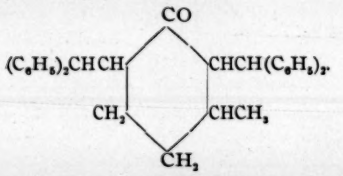
Analysis:

I. 0.1420 gram substance (176°) gave 0.4248 gram CO_2 and 0.0868 gram H_2O.

II. 0.12279 gram substance (142°) gave 0.3830 gram CO_2 and 0.0786 gram H_2O.

	Calculated for $C_{27}H_{26}O_3$.	Found. I.	II.
C	81.41	81.58	81.66
H	6.53	6.78	6.82

Tetraphenyltrimethylcyclohexanone,



—The 2 isomeric ketones described above react with ethereal phenylmagnesium bromide at the ordinary temperature, and both give the same products. The ethereal solution obtained by decomposing the magnesium derivatives was allowed to stand in a closed separating funnel for several days, then filtered and the filtrate evaporated to small volumes. The solid that separated in the funnel was purified by recrystallization from benzene, which deposited it in fine needles, melting at 282°. The substance is almost insoluble in boiling absolute alcohol, sparingly in boiling acetone and chloroform, moderately in hot benzene. A second product separated

from the filtrates. This was purified by recrystallization from absolute alcohol. It separated in long, silky needles melting at 190°; readily soluble in alcohol, ether and chloroform.

Analyses:

I. 0.1227 gram substance (282°) gave 0.4010 gram CO_2 and 0.0790 gram H_2O.

II. 0.1214 gram substance (190°) gave 0.3961 gram CO_2 and 0.0758 gram H_2O.

	Calculated for $C_{28}H_{28}O$.	Found. I.	Found. II.
C	89.18	89.03	88.98
H	7.21	7.14	6.94

The analyses show that the substances are isomeric. Tests with an acetone solution of potassium permanganate indicated that both are saturated and tests with ethylmagnesium bromide proved the absence of hydroxyl groups. The substances are, therefore, saturated ketones and, since structural isomerism is impossible, they are, doubtless, stereoisomers. It is noteworthy that neither of the ketones reacts with phenylmagnesium bromide in boiling ethereal solution, the groups around the carbonyl interfering with the reaction in the same way that they do in benzpinacolin and similar compounds.

Experiments with Benzaldiketohydrindene.

The ketone was made by heating diketohydrindene with excess of benzaldehyde[1] to 120°. The product was ground up with absolute alcohol, filtered and recrystallized from ethyl acetate. When the finely powdered solid is added, in very small portions, to ethereal phenylmagnesium bromide it first imparts a brilliant red color to the solution, then produces a permanent red precipitate. This precipitate interferes with the reaction because it protects the sparingly soluble ketone from the reagent. The most satisfactory procedure was as follows: A solution of the ketone in boiling benzene was added, in small portions, to a boiling solution of the reagent and the resulting dark red liquid boiled for an hour

[1] Ann. Chem. (Liebig), **252**, 75.

to complete the reaction. The magnesium derivative was decomposed with iced acid, the yellow benzene-ether layer removed and distilled with steam until diphenyl could no longer be detected in the distillate. The orange-colored residue was washed with a small quantity of cold alcohol, then dissolved in boiling absolute alcohol. The substance separated in quinone-yellow plates, melting at 162°.

Analyses:

I. 0.1410 gram substance gave 0.4665 gram CO_2 and 0.0630 gram H_2O.

II. 0.1188 gram substance gave 0.3923 gram CO_2 and 0.0538 gram H_2O.

	Calculated for $C_{28}H_{14}O$.	Found. I.	Found. II.
C	89.95	90.23	90.08
H	4.76	5.04	5.03

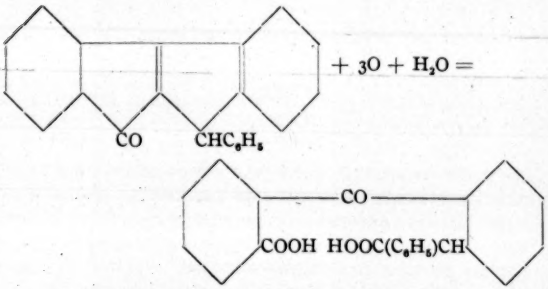
The substance is readily soluble in chloroform, moderately in acetone and ethyl acetate, sparingly in alcohol. Concentrated sulphuric acid first turns it red, then dissolves it, forming a dark green solution. In acetone solution it readily reduces potassium permanganate. The principal oxidation product is an acid. This was purified by recrystallization from a mixture of ether and low-boiling ligroin. It was deposited in aggregates of flat, colorless needles, melting at 131°–133°. It is very readily soluble in alcohol and ether, sparingly soluble in ligroin.

Analysis:

0.1238 gram substance gave 0.3341 gram CO_2 and 0.0500 gram H_2O.

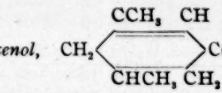
	Calculated for $C_{28}H_{16}O_3$.	Found.
C	73.33	73.44
H	4.44	4.48

The formation of this acid establishes the formula of the ketone. The oxidation is represented by the equation:



A convenient name for a hydrocarbon with the carbon skeleton contained in the ketone would be "bindene." The ketone itself would then be 6-phenylbindenone-8.

Experiments with Dimethylcyclohexenone and Benzaldimethylcyclohexenone.

Phenyldimethylcyclohexenol,  —

Knoevenagel and Lange[1] found that when hydrocyanic acid combines with dimethylcyclohexenone, the addition takes place at the ethylene linkage and the product is a saturated ketone. The following experiment shows that when phenylmagnesium bromide combines with the same ketone the addition is to carbonyl and the product is a tertiary alcohol. Twenty-five grams of the ketone were added slowly to a well cooled solution of phenylmagnesium bromide and the mixture allowed to stand for 10 hours. The resulting magnesium derivative was decomposed in the usual way and the ethereal solution allowed to evaporate. The product separated in large, colorless plates. After one crystallization from a mixture of ether and low-boiling ligroin the substance melted sharply at 111°. The yield of pure product was 36 grams.

[1] Ber. d. chem. Ges., 37, 407.

Analysis:

0.1385 gram substance gave 0.4240 gram CO_2 and 0.1140 gram H_2O.

	Calculated for $C_{14}H_{18}O$.	Found.
C	83.2	83.48
H	8.9	9.14

For the purpose of distinguishing between ketone and tertiary alcohol an ethereal solution containing 5 grams of the substance was added to excess of ethylmagnesium bromide. The reaction was accompanied by a steady evolution of gas and 4.4 grams of the original substance was recovered when the magnesium derivative was decomposed with ice and acid. The product is, therefore, a tertiary alcohol. It is readily soluble in all organic solvents except ligroin, combines with bromine and reduces potassium permanganate at the ordinary temperature.

Benzaldimethylcyclohexenone.—Knoevenagel and Klages[1] condensed benzaldehyde and dimethylcyclohexenone in the presence of a large quantity of very dilute alcohol. The following procedure is more satisfactory because it can be completed in much shorter time and yields a purer product. A mixture of 50 grams of benzaldehyde and the same weight of ketone is diluted with an equal volume of alcohol. This solution is cooled with ice-water, then treated with 20 grams of a 10 per cent solution of sodium hydroxide and placed in an ice chest. In the course of an hour or two the liquid separates into 2 layers. A speck of solid ketone, added at this stage, induces a slow crystallization of almost pure product. The mixture is allowed to remain in the ice chest for 8 hours, then filtered, the solid washed with alcohol and water, and purified by recrystallization from alcohol. From the filtrate, which is returned to the ice chest, a considerable quantity of less pure product separates in the course of 24 hours. The total yield of pure substance is from 70 to 75 per cent of the calculated amount.

When dibenzaldimethylcyclohexenone is added to ethereal

[1] Ann. Chem. (Liebig), 281, 118.

phenylmagnesium bromide it produces the usual intermediate colored precipitate. This slowly dissolves on shaking and gives rise to a voluminous, colorless precipitate that interferes with the reaction by protecting the intermediate compound from further action of the reagent. It is necessary, therefore, to use a large excess of the reagent and to boil the mixture until all trace of color has disappeared. It is requisite, also, to decompose the magnesium compound at as low a temperature as possible, otherwise the result is an oil that does not solidify in a freezing mixture and does not distil under diminished pressure without decomposition. If the magnesium derivative is poured, slowly, into a freezing mixture of ice and concentrated hydrochloric acid and the ethereal layer first washed with ice water and then diluted with low-boiling ligroin, the product is a colorless solid. The impure solid slowly passes into oil, but it can be purified with slight loss by recrystallization from ether, and the pure substance is stable at the ordinary temperature. It crystallizes in large, lustrous tables, is readily soluble in organic solvents except ligroin and melts at 106°.

Analysis:

I. 0.1365 gram substance gave 0.4110 gram CO_2 and 0.0995 gram H_2O.

II. 0.1262 gram substance gave 0.3775 gram CO_2 and 0.5930 gram H_2O.

	Calculated for $C_{21}H_{24}O_2$.	Found. I.	II.
C	81.82	82.11	81.61
H	7.79	8.09	8.11

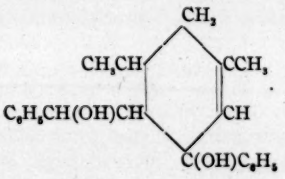
A product formed by the addition of a molecule of ethylmagnesium bromide to benzaldimethylcyclohexenone would have the formula $C_{21}H_{22}O$; the substance differs from this by 1 molecule of water, which is probably added when the magnesium derivative is decomposed.

The behavior of the substance towards ethylmagnesium bromide shows that it, in all probability, contains 2 hydroxyl groups. Twelve grams (1 mol.) were added to a solution of ethylmagnesium bromide made from 1 gram—

slightly more than 2 atoms—of magnesium. Effervescence stopped before quite all of the solid had been introduced and there was no evolution of gas when the magnesium derivative was decomposed with iced acid. The magnesium compound appeared to be the same that was obtained in the original reaction. When decomposed, it gave a little over 10 grams of the substance melting at 106°. The product, therefore, reacts with 2 molecules of ethylmagnesium bromide, but no addition takes place, indicating the absence of carbonyl and the presence of 2 hydroxyl groups.

The substance readily reduced potassium permanganate dissolved in acetone. The acetone, on evaporation at the ordinary temperature, left only a minute quantity of oil, showing that there are no neutral oxidation products. The salts were dissolved in water, the solution acidified and the acids extracted with ether. The ether, on evaporation, left an oil that partially solidified in a freezing mixture. By exhaustive extraction with cold, low-boiling ligroin it was possible to remove all of the solid without dissolving more than a trace of oil. The ligroin, on evaporation, left almost pure benzoic acid. Thirteen grams of substance gave 6.4 grams of benzoic acid—almost exactly 1 molecule for 1 of the substance.

It has not been possible, thus far, to get either the oily acid or any of its derivatives sufficiently pure for analysis. Nor has it been possible to find any other reaction that would give more definite information as to the nature of the product $C_{21}H_{24}O_2$. Its structure is, therefore, uncertain, but the most probable formula is



Experiments with Diphenylcyclohexenone.

(IN PART BY MARY VIOLET DOVER.)

Most of the unsaturated ketone used in the following experiments was made according to directions by Knoevenagel and Schmidt.[1] As this method does not give a satisfactory yield we tried the condensation at low temperatures and in the presence of a small quantity, instead of 1 equivalent, of sodium alcoholate. We found that, under these conditions, the reaction consists in the addition of a molecule of acetoacetic ester to one of benzalacetophenone, just as it does when diethylamine is used as a condensing agent. The differences observed by Knoevenagel[2] when he used sodium alcoholate and diethylamine for bringing about the same reaction are, therefore, not to be ascribed to the specific properties of the condensing agent, but to the differences in the amounts of these agents used and to the temperatures at which the condensations were effected.

The addition product obtained when sodium alcoholate is used is, however, not identical but isomeric with that obtained with diethylamine. The procedure was as follows: A solution of 0.5 gram of sodium, in a little absolute alcohol, was added to 30 grams of benzalacetophenone and 15 grams of acetoacetic ester, dissolved in 100 cc. of absolute alcohol, and the mixture placed in an ice chest. Long white needles of the product began to separate in a short time and the condensation was complete in 24 hours. The solid was purified by means of alcohol. It is readily soluble in boiling alcohol, sparingly soluble in cold alcohol and in ether. It crystallizes in colorless needles, melting at 168°. In agreement with Knoevenagel we found that the product obtained when diethylamine is used as condensing agent melts at 121°.

Analysis:

0.1652 gram substance gave 0.4520 gram CO_2 and 0.0946 gram H_2O.

[1] Ann. Chem. (Liebig), **281**, 59.
[2] Ber. d. chem. Ges., **35**, 397.

	Calculated for $C_{21}H_{20}O_4$.	Found.
C	74.55	74.63
H	6.50	6.35

Thirty grams of benzalacetophenone gave 34.5 grams of pure product. The substance is evidently closely related to that obtained by using diethylamine, as both give the same cyclic ester when heated with sodium alcoholate. As the product is a β-ketonic ester containing 2 unequal, asymmetric carbon atoms, the 2 substances may be either structural or spatial isomers. There is no advantage in carrying out the reaction in steps, as the loss of material takes place during the closing of the ring. These 4 grams of the substance, boiled for an hour with 0.4 gram sodium, dissolved in 25 cc. of absolute alcohol, yielded only 2.7 grams of diphenylcarboxethylcyclohexenone, melting at 111°.

The ketone that we obtained by hydrolyzing the cyclic ester, as directed by Knoevenagel and Schmidt and recrystallizing the product from alcohol, had a considerably higher melting point than that given by these authors —83° instead of 70°–72°. That it was pure diphenylketocyclohexenone is shown by the following analysis:

0.2016 gram substance gave 0.6434 gram CO_2 and 0.1196 gram H_2O.

	Calculated for $C_{18}H_{16}O$.	Found.
C	87.1	87.00
H	6.4	6.54

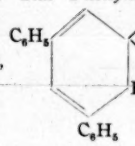
For the purpose of future identification, we made the oxime by heating an alcoholic solution of the ketone with hydroxylamine hydrochloride and powdered sodium carbonate. The oxime crystallizes in needles, melting at 163°–164°, is readily soluble in alcohol, sparingly in ether, insoluble in water.

Analysis:

0.1367 gram substance gave 0.5088 gram CO_2 and 0.0989 gram H_2O.

	Calculated for $C_{18}H_{17}ON$.	Found.
C	82.13	81.8
H	6.3	6.42

Reaction with Phenylmagnesium Bromide: Triphenyldihydrobenzene,



.—The finely powdered ketone was added, gradually, to excess of phenylmagnesium bromide and the mixture allowed to stand for 12 hours. The new magnesium derivative separated in the form of colorless crystals. It was decomposed with iced acid, the ethereal layer evaporated and the solid residue recrystallized from alcohol.

0.1608 gram substance gave 0.5508 gram CO_2 and 0.0947 gram H_2O.

	Calculated for $C_{24}H_{20}$.	Found.
C	93.5	93.40
H	6.5	6.52

The substance is a hydrocarbon, evidently formed by loss of water from a tertiary alcohol. It readily reduced a solution of potassium permanganate at the ordinary temperature, the sole product of oxidation being another hydrocarbon which, after crystallization from chloroform, melted at 172°.

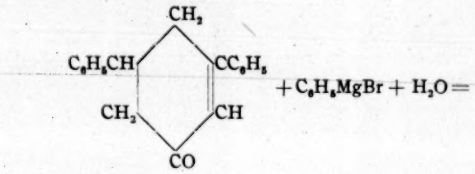
Analysis:

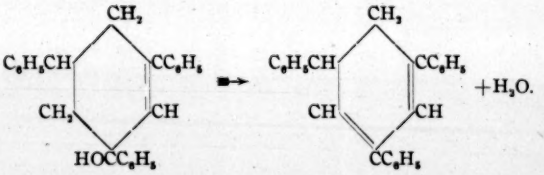
0.1572 gram substance gave 0.5461 gram CO_2 and 0.0856 gram H_2O.

	Calculated for $C_{24}H_{18}$.	Found.
C	94.1	94.07
H	5.9	6.04

The oxidation product has the composition and almost the melting point given for 1,3,5-triphenylbenzene. It was

completely identified by comparison with a specimen of *sym*triphenylbenzene, made by condensing acetophenone. The product of the reaction with phenylmagnesium bromide is, therefore, triphenyldihydrobenzene:





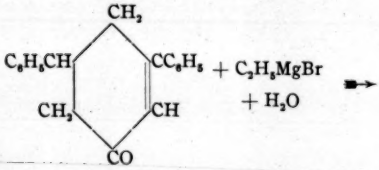
Triphenyldihydrobenzene crystallizes in colorless needles that melt at 111°. It is readily soluble in acetone and chloroform, moderately in alcohol and ether. The yield of pure product was 87 per cent of the calculated quantity.

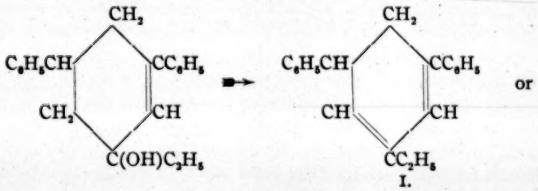
Reaction with Ethylmagnesium Bromide.—The procedure was the same as that described under phenylmagnesium bromide. The product, isolated in the usual way, was an oil that was evidently a mixture. By repeated distillation under diminished pressure it was separated into 2 fractions, the one boiling at 152° (22 mm.), the other 153°–158° (22 mm.). The fraction boiling at 152° gave the following analytical results:

0.1331 gram substance gave 0.4492 gram CO_2 and 0.0934 gram H_2O.

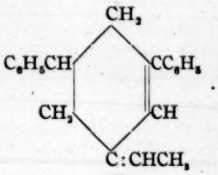
	Calculated for $C_{24}H_{20}$.	Found.
C	93.2	93.04
H	7.7	7.79

There are only 2 possible formulas for this hydrocarbon:





I.



II.

For the purpose of distinguishing between these formulas the hydrocarbon was oxidized with potassium permanganate, dissolved in acetone. The product was an acid, melting at 155°–157°.

Analysis:

0.1337 gram substance gave 0.3712 gram CO_2 and 0.0696 gram H_2O.

	Calculated for $C_{17}H_{16}O_2$.	Found.
C	76.1	75.7
H	6.0	5.8

As it was difficult to get an acid with a perfectly sharp melt-

ing point we confirmed the formula by an analysis of the methyl ester, obtained by saturating a methyl alcoholic solution of the acid with hydrogen chloride. The ester crystallized in stout needles, melting at 94°.

Analysis:

0.1260 gram substance gave 0.3527 gram CO_2 and 0.0730 gram H_2O.

	Calculated for $C_{15}H_{18}O_3$.	Found.
C	76.6	76.26
H	6.4	6.42

A hydrocarbon with the structure represented by I. might be oxidized either to ethyldiphenylbenzene or to α-phenyl-β-benzoylpropionic acid, while a hydrocarbon with the structure represented by II. would be expected to give β-phenyl-γ-benzoylbutyric acid. We made the latter in accordance with the directions given by Vorländer and Knotsch and identified both our acid and its methyl ester. The hydrocarbon is, therefore, ethylidenediphenyltetrahydrobenzene.

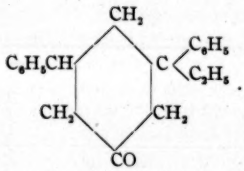
The fraction boiling at 152°–168° was a mixture of the hydrocarbon just described and a substance indifferent to potassium permanganate. As it could not be completely separated it was oxidized in solution in acetone. The hydrocarbon was destroyed, the resulting potassium salt being deposited with the oxides of manganese, while the indifferent compound remained in solution. By evaporating the acetone and distilling the oily residue under diminished pressure, the substance was obtained in pure condition—a colorless oil boiling at 170° (24 mm.).

Analysis:

0.1313 gram substance gave 0.4142 gram CO_2 and 0.0963 gram H_2O.

	Calculated for $C_{20}H_{22}O$.	Found.
C	86.33	86.03
H	7.94	8.15

The indifference to permanganate shows that this substance is the saturated ketone—ethyldiphenylcyclohexanone,



In order to determine whether the ketone was formed by direct addition to the ethylene linkage, or by 1,4-addition, the reaction with ethylmagnesium bromide was repeated, but instead of allowing the ethereal solution to stand it was immediately evaporated in a rapid stream of oxygen. The residue partially solidified in a freezing mixture. The oil was removed, the solid washed with ligroin and repeatedly recrystallized from a mixture of chloroform and ether. It was thus obtained in small, hard prisms, melting, with decomposition, at 269°–270°; sparingly soluble in alcohol and ether, moderately in acetone; readily in chloroform.

Analysis:

0.1269 gram substance gave 0.3615 gram CO_2 and 0.0845 gram H_2O.

	Calculated for $C_{20}H_{22}O_2$.	Found.
C	77.4	77.69
H	7.01	7.39

The substance is ethyldiphenylcyclohexenol peroxide, as represented in the introduction. Its production proves that when ketones are formed by the action of Grignard's reagent on unsaturated cyclic ketones the result is due to 1,4-addition.

The above-mentioned products—hydrocarbon and ketone—were obtained by using a large excess of ethylmagnesium bromide. When unsaturated ketone and magnesium derivatives are used in equivalent quantities the result is somewhat different. The same hydrocarbon is produced, in approximately the same amount, but in place of the ketone there is a complex product quite similar to the substances obtained from

open-chained unsaturated ketones. The product separated in the solid form when the magnesium derivatives were decomposed with iced acid. It was purified by recrystallization from chloroform and was deposited in fine needles, melting at 256°.

Analysis:

0.1441 gram substance gave 0.4560 gram CO_2 and 0.0972 gram H_2O.

	Calculated for $C_{28}H_{28}O_2$.	Found.
C	86.69	88.30
H	7.22	7.51

The composition indicates that the substance is formed by the addition of a molecule of unsaturated ketone to the primary product, but not much reliance can be placed on conclusions drawn from the analytical results obtained from these complex substances.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE.

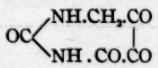
Contributions from the Sheffield Laboratory of Yale University.

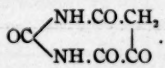
CXLII.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF URACIL-5-CARBOXYLIC ACID.

[NINETEENTH PAPER.]

BY HENRY L. WHEELER, TREAT B. JOHNSON, AND CARL O. JOHNS.

A new substance, having acid properties, called orotic acid (*Acido orotico*) has been isolated by Biscaro and Belloni[1] from milk. They assign to this compound the empirical formula, $C_5H_4O_4N_2.H_2O$, and believe that its structure is to be represented by one of the following formulas:

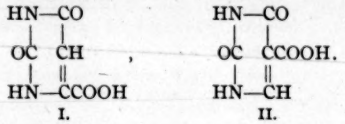




[1] Annuario della Soc. Chimica di Milano, XI, fasc. I (1905); *Ibid.*, XI, fasc. II (1905) *Vide* also Centrabl., 1905, I, 63, 64. We take this occasion to thank the above authors for sending us reprints of these two articles.

It seemed to us that instead of a ring with 7 members, one with 5 or 6 would most probably prove to be correct. The properties of the substance and the fact that it gives urea on oxidation, suggested that it might be a pyrimidine.

The above empirical formula is that of a uracil carboxylic acid having a molecule of water of crystallization. There are 2 uracil carboxylic acids which have the acid group attached to carbon, namely, the 4- (I.) and 5- (II.) derivatives,



I. II.

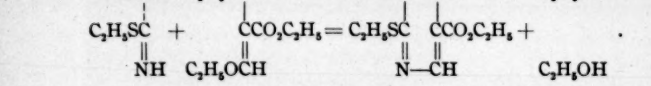
As neither of these acids have hitherto been prepared, a description is now given of the preparation and properties of the latter acid, while an account of uracil-4-carboxylic acid will appear in a later article. The study of these acids, and also the carboxyl derivatives of thymine and cytosine, is of interest on account of the possibility that in the nucleic acids uracil, thymine and cytosine may exist as carboxyl derivatives, being held together not alone by means of phosphorus atoms, as suggested by Bang[1] and Osborne and Harris,[2] but also by an acid amide or polypeptide grouping as in the case of the proteids. In such an event the means hitherto used to disrupt the nucleic acid molecule must also cause a loss of the carboxyl group from the pyrimidines. In this connection it is interesting to note that uracil-4-carboxylic acid can be heated with 20 per cent sulphuric acid, at 160°–170°, without alteration while, by such treatment, uracil-5-carboxylic acid is quantitatively converted into uracil. In fact, simply on prolonged boiling of this acid with hydrochloric acid it is converted into uracil. Uracil may, therefore, exist in the nucleic acids as a 5-carboxyl compound. We have shown that the pseudothioureas, $H_2NC(SR) : NH$, will react with aldehyde[3]

[1] Z. physiol. Chem., **31**, 425 (1900).
[2] Conn. Exper. Sta. Rep., 1901, p. 418.
[3] THIS JOURNAL, **29**, 480 (1903).

and ketone esters to form pyrimidines in cases where urea refuses to act. According to Behrend the alkyl acetoacetic esters do not condense with urea.[1] We found that the methyl and ethyl derivatives give pyrimidines with the pseudothioureas. In that article we described 4,5-dimethyluracil as new, having missed the fact that Schlenker had obtained this substance by a different method.[2]

Another striking example of the difference between urea and a pseudothiourea was found when we tried the behavior of Claisen's ethoxymethylenemalonic ester[3] toward these compounds. Urea showed no sign of reacting at 140° and a condensation was not effected on standing in alkaline solutions.

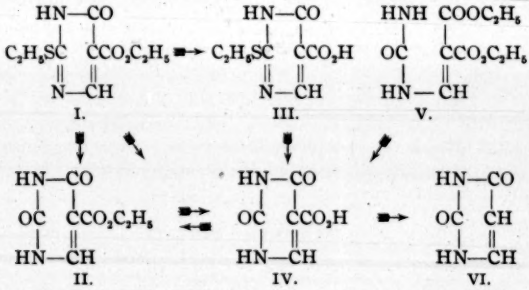
On the other hand, when ethoxymethylenemalonic ester was added to an alkaline, aqueous solution of ethylpseudothiourea hydrobromide,[4] an immediate reaction took place and a salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine separated. This condensation can be represented as follows:



2-Ethylmercapto-5-carbethoxy-6-oxypyrimidine (I. see below) can be converted directly into uracil-5-carboxylic acid (IV.) by simply boiling with aqueous hydrochloric acid. When the mercapto ester (I.) is boiled, in alcoholic solution, with a small quantity of hydrochloric acid, uracil-5-ethylcarboxylate (II.) results. And this, on saponification, gives uracil-5-carboxylic acid. On the other hand, warm alkalies saponify the mercapto ester (I.) and give 2-ethylmercapto-5-carboxyl-6-oxypyrimidine (III.), which, with hot hydrochloric acid, gives uracil-5-carboxylic acid (IV.). When the acid (IV.) is melted it gives uracil (VI.).

[1] Ann. Chem. (Liebig), **229**, 16 (1885).
[2] Ber. d. chem. Ges., **34**, 2812 (1901).
[3] Ann. Chem. (Liebig), **297**, 75 (1897).
[4] This Journal, **29**, 483 (1903).

The formation of uracil, in this manner and also on heating with acids, shows that the condensation took place as represented in the above equation and that the product (I.) is not a barbituric acid derivative. In fact, we have not yet observed a satisfactory condensation of malonic ester, or any of its derivatives, with the pseudothioureas to form barbituric acid derivatives. The substance represented by Formula V., uramidomethylenmalonic ester, was occasionally found as a by-product in the mother liquors of the condensation. On saponification it gave uracil-5-carboxylic acid. These compounds and their transformations can be represented as follows:



In some respects the properties of uracil-5-carboxylic acid agree closely with those of orotic acid. It is difficultly soluin water, difficultly or insoluble in organic solvents and it crystallizes with the required 1 molecule of water of crystallization. Orotic acid is said to decompose at 260°. Our acid melts, with decomposition, at 278°. The potassium salt that crystallizes from solutions containing an excess of alkali is a monopotassium salt, $C_5H_3O_4N_2K$. Like orotic acid, our acid is dibasic and forms 2 series of salts. The potassium salt gives precipitates with barium chloride (crystalline), lead acetate and silver nitrate.

On the other hand, uracil-5-carboxylic acid differs from

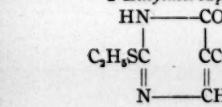
orotic acid as follows: It does not give a monosilver salt having the composition $C_5H_3O_4N_2Ag.H_2O$, which Biscaro and Belloni state is formed when silver nitrate is added to a solution of the monopotassium salt. In our case, when the monopotassium salt or alkali, acid and silver nitrate, in the proportion 1:1:1 were used, the silver salt formed was a disilver salt, a corresponding amount of acid remaining in the filtrate.

When methyl iodide was allowed to react, under pressure, on either mono or disilver orotate, Biscaro and Belloni obtained a monomethyl derivative melting at 248°–250°. When we heated our silver salt with methyl iodide, in a closed tube at 100°, we obtained a mixture of substances from which a dimethyl derivative, melting about 254°–256°, was isolated. Their monoethyl ester melted at 200°; our product, obtained in like manner from the silver salt, melted at 162°–163, and the analysis showed that it was a diethyl derivative.

The free uracil-5-carboxylic acid does not give a precipitate with barium chloride, and we were unable to obtain a dichloride, which could be crystallized from boiling water without reverting to the acid, when the potassium salt was heated with phosphorus oxychloride.

EXPERIMENTAL PART.

2-Ethylmercapto-5-carbethoxy-6-oxypyrimidine,



C_2H_5SC (double bond) N — CH; HN — CO; $CCO_2C_2H_5$.—The best results in the preparation of this substance were obtained as follows: Fifty-four grams of ethoxymethylenemalonic ester were added to a solution of 50 grams of ethylpseudothiourea hydrobromide in 50 cc. of water. To this mixture 30 grams of potassium hydroxide were slowly added and the solution was kept cold. The addition of alkali produced a yellow color and the solution became semisolid from the separation of a bulky, yellow precipitate. This impure potassium salt, when dry, weighed 58 grams, the yield being 87 per cent of the calculated, theory

requiring 66.5 grams. It crystallized from water in the form of colorless prisms and from alcohol in needles.

When a strong aqueous solution of the potassium salt was treated with dilute hydrochloric acid, avoiding an excess of acid, 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine separated as a white, crystalline precipitate. This substance is readily soluble in hot alcohol and it separates in the form of long, slender, colorless prisms; from water it forms long, bulky, asbestos-like needles. It melts at 131° to a clear oil and it gave the following results on analysis (Kjeldahl):

	Calculated for $C_9H_{12}O_4N_2S$.	Found. I.	II.
N	12.23	12.02	12.28

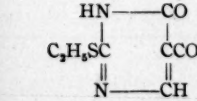
This ester dissolves in cold hydrochloric acid and is reprecipitated by ammonia. It has both acid and basic properties.

Uramidomethylenemalonic Ester, $H_2NCONHCH : C(CO_2C_2H_5)_2$. —This substance was obtained, in 2 experiments, by precipitating with hydrochloric acid, the filtrate from which the potassium salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine had separated. In the above case the amount obtained was 4.8 grams. It is very difficultly soluble in boiling water, readily soluble in hot alcohol; when crystallized from 50 per cent alcohol it forms bunches of colorless prisms melting at 206°, with effervescence. Nitrogen determinations gave (Kjeldahl):

	Calculated for $C_9H_{14}O_5N_2$.	Found. I.	II.
N	12.17	12.22	12.06

This material has acid properties. When warmed with alkali, saponification takes place and hydrochloric acid then precipitates uracil-5-carboxylic acid.

2-Ethylmercapto-5-carboxyl-6-oxypyrimidine,



C_2H_5SC ‖ CCO_2H. —Ten grams of the potassium salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine were dissolved

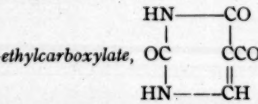
in hot alcohol and a hot solution of 4.3 grams of potassium hydroxide, in a little water, were added. Saponification took place immediately and the solution became a thick jelly. The alcohol was then evaporated and the residue taken up in a little water. On adding an excess of hydrochloric acid a white precipitate of the mercapto acid separated. It weighed 7.1 grams, while the calculated is 7.5 grams, the yield being 94.6 per cent of theory.

This acid dissolves readily in hot alcohol, less readily in hot water, from which solvent it forms bunches of colorless, sharp-cornered plates. It melts to a clear oil at 167° and effervesces at a higher temperature. Nitrogen determination:

	Calculated for $C_7H_8O_2N_2S$.	Found.
N	14.00	13.72

This acid appears to be stronger than acetic acid, since it was not liberated from its potassium salt by means of an excess of acetic acid. It gives a bulky, white, gelatinous precipitate with alkali and silver nitrate. When warmed with hydrochloric acid, it readily evolves mercaptan and gives uracil-5-carboxylic acid.

Uracil-5-ethylcarboxylate,



— Ten grams of the potassium salt of 2-ethylmercapto-5-carbethoxy--6 oxypyrimidine were dissolved, or suspended, in about 75 cc. of strong alcohol, and about 5 cc. of concentrated hydrochloric acid were added. The whole was then boiled with a return condenser for several hours; the alcohol was evaporated and the residue was taken up in about 60 cc. of warm water. The hydrochloric acid was neutralized with ammonia and the solution was then filtered hot. On adding an excess of strong ammonia to the filtrate the ammonium salt of uracil-5-ethyl-carboxylate separated as a sponge-like mass of long, slender, colorless needles. This was dissolved in about 50 cc. of water by warming and then a slight excess of acetic acid was added.

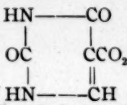
On cooling, a granular, crystalline precipitate of the free ester separated. This was found to be very soluble in hot water and moderately so in cold. It was difficultly soluble in alcohol. When crystallized from water it formed flat, sharp-pointed prisms, melting at 236°–237°. Analysis:

	Calculated for $C_7H_8O_4N_2$.	Found. I.	II.
N	15.21	15.09	15.21

The *ammonium salt* of uracil-5-ethylcarboxylate is characterized by some peculiar properties. When a not too dilute solution of the ester is treated with a little strong ammonia, long, slender needles of the ammonium salt form at once. The vapor from a rod dipped in ammonia and held above the surface of an aqueous solution of the ester will cause crystals to form. When a solution of the salt is boiled, ammonia escapes and, on cooling, nothing separates until more ammonia is added. If the solution is concentrated by heating, the free ester separates. The ammonium salt is insoluble, or difficultly soluble in alcohol. An aqueous solution of the ester was precipitated with ammonia and the precipitate was dried over calcium chloride. The needles thus obtained melted at about 220° to an oil that effervesced. Nitrogen determination (Kjeldahl):

	Calculated for $C_7H_8O_4N_2.NH_3.H_2O$.	Found.
N	19.13	19.33

When uracil-5-carboxylic ethyl ester is warmed with aqueous hydrochloric acid it is readily saponified and uracil-5-carboxylic acid is obtained.



Uracil-5-carboxylic Acid, $CCO_2H.H_2O$. — This acid can be prepared directly from the condensation product of ethoxymethylenemalonic ester and ethylpseudothiourea hydrobromide, or, in other words, from the potassium salt of 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine, without the

isolation of the above intermediate products, by simply dissolving the salt in a moderate amount of strong hydrochloric acid and evaporating to dryness on the steam-bath. If the product contains sulphur, the operation is repeated. The residue is then crystallized from water as the acid is practically insoluble in alcohol. It is difficultly soluble in water and separates in the form of colorless, characteristic, minute pyramids with rough faces. Or small prisms form, the faces sometimes alternating with those of a pyramid. The crystals contain $1H_2O$, which is given off on heating above 100°. The acid melts partially, but quite sharply, at 278°, with energetic efferyescence. The aqueous solution reddens litmus and it gives no immediate precipitate with lead or copper acetate, or barium chloride. Analysis:

I. 0.5002 gram substance, dried at about 50°, lost 0.0502 gram of water when heated for 1 hour at 122°

II. 0.5486 gram substance lost 0.0561 gram water when heated for 2 hours at 105°–110°.

	Calculated for $C_5H_4O_4N_2.H_2O$.	Found. I.	II.	III.
H_2O	10.34	10.03	10.22	10.02
N	16.09	16.15	16.03	16.26

Nitrogen determination of the anhydrous acid:

	Calculated for $C_5H_4O_4N_2$.	Found. I.	II.	III.
N	17.94	17.88	17.99	17.91

Nitrogen was determined by Kjeldahl's method except in Analysis III. The acid used for Analysis III. (water) and Analysis VI. was obtained by the saponification of uramidomethylenemalonic ester. The other samples were obtained from the potassium salt described above.

Behavior on Heating.—About 0.5 gram of the acid was heated in a test tube, immersed in a sulphuric acid bath, at a temperature a little above its melting point until effervescence ceased. The dark-colored product was boiled with water and animal charcoal and the solution concentrated. On cooling, the characteristic crystals of uracil separated, melting or effervescing at 335°. Analysis (Kjeldahl):

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.00	24.89

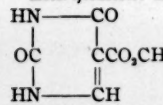
Action of Acids: Formation of Uracil.—The action of 20 per cent sulphuric acid was tried as follows: Fifty-five-hundredths gram of the acid potassium salt of uracil-5-carboxylic acid was sealed in a tube with 5 cc. of sulphuric acid, sp. gr. = 1.15, and heated at 160°–169° for 2 hours. On opening the tube, carbon dioxide escaped and the minute microscopic needles that had separated, after washing with water, were found to melt at 336° without further purification. A nitrogen determination agreed with the calculated for uracil:

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.00	24.97

The needles weighed 0.25 gram, which amount is 71 per cent of the calculated, or, allowing for solubility, it is practically a theoretical yield.

The Action of Concentrated Hydrochloric Acid.—One gram of uracil-5-carboxylic acid was boiled with about 50 cc. of concentrated hydrochloric acid, using a return condenser, for 18 hours. The acid was then evaporated and the residue was crystallized from water, whereupon over 0.3 gram of uracil separated.

Esterification: Methyl Uracil-5-carboxylate,



—When uracil-5-carboxylic acid is warmed with acids in methyl or ethyl alcohol, it is smoothly esterified. One gram of the anhydrous acid was suspended in 75 cc. of methyl alcohol, to which 5 drops of concentrated sulphuric acid had been added. On boiling for 8 hours, all of the acid went into solution and on evaporation to a small volume a gelatinous mass was formed. This gave a white powder when stirred with cold water. The material thus obtained was readily soluble in hot water and on cooling, short, stout, color-

less prisms separated. These sintered at about 225° and decomposed at 233°. Nitrogen determination (Kjeldahl):

	Calculated for $C_5H_4O_4N_2$.	Found. I.	Found. II.
N	16.47	16.62	16.58

When uracil-5-carboxylic acid was warmed with ethyl alcohol and sulphuric acid, the ethyl ester described above was obtained. It was identified by the melting point 236° and by its behavior towards ammonia.

The Acid Potassium Salt, $C_5H_3O_4N_2K.C_5H_4O_4N_2$.—When uracil-5-carboxylic acid and either sodium or potassium hydroxide were mixed, in molecular proportions, the hot aqueous solution, on cooling, deposited an acid salt. For example, 8 grams of the hydrous acid and 2.5 grams of potassium hydroxide were dissolved in about 500 cc. of boiling water. On cooling, 2 grams of slender, needle-like crystals separated. These effervesced at about 270°. Analysis:

	Calculated for $C_{10}H_7O_8N_4K$.	Found. I.	Found. II.	Found. III.
N	16.00	15.89	15.98	.....
K	11.14	.....	.....	10.87

The Monopotassium Salt, $C_5H_3O_4N_2K$.—Three grams of uracil-5-carboxylic acid were dissolved in a solution of 2 grams of potassium hydroxide, 1.9 grams = 2 mols., in about 20 cc. of water; on concentrating on the steam-bath small needles separated. These were dried at about 55°. Nitrogen determinations (Kjeldahl):

	Calculated for $C_5H_4O_4N_2.K_2$.	Calculated for $C_5H_3O_4N_2K$.	Found. I.	Found. II.
N	12.06	14.43	14.72	14.71

The analyzed material showed no signs of melting at 295°. On dissolving the dried salt in water the solution was found to be neutral to litmus and turmeric. It gave a white, insoluble precipitate with lead acetate and the hot solution gave a crystalline precipitate with barium chloride.

The Barium Salt, $(C_5H_3O_4N_2)_2Ba$.—Barium chloride was added, in excess, to a hot, dilute, neutral solution of the above

potassium salt. Stout, microscopic prisms, pointed at both ends, crystallized out. These were almost insoluble in hot water. They were dried at 110°–120° but did not give off water.

	Calculated for $C_{10}H_6O_8N_4Ba$.	Found.
Ba	30.64	28.83

The Silver Salt.—Two grams of the monopotassium salt were dissolved in 100 cc. of water and 1.7 grams of silver nitrate in 50 cc. of water were slowly added, with stirring, in order to prevent a local excess of the nitrate. A white, bulky, gelatinous precipitate separated which did not alter or become granular on warming. The solution was diluted with 100 cc. of water and allowed to settle; the precipitate was washed by decantation and then filtered on cheese cloth. It was dried at 100° for analysis.

One molecular proportion more of silver nitrate was then added to the filtrate. This gave a slight precipitate. On adding 0.5 gram of potassium hydroxide, in a little water, a quantity of white salt was again precipitated, apparently equal in amount to that which was obtained at first. The analytical results did not agree with those calculated for a pure salt. They indicate that the precipitate was a mixture of a mono- and a disilver salt. A sample prepared by taking molecular proportions of acid, sodium hydroxide and silver nitrate gave no better results (Analyses III. and IV.).

	Calculated for $C_5H_3O_4N_2Ag$.	Calculated for $C_5H_2O_4N_2Ag_2$.	Found. I.	II.	III.	IV.
N	10.64	7.56	8.86	8.54	....	....
Ag	41.64	58.37	....	....	49.0	51.5

The following shows that uracil-5-carboxylic acid gives a disilver salt: Eleven grams of the acid, dissolved in water and treated with 2 molecules of sodium hydroxide and 2 molecules of silver nitrate, gave a pure white precipitate which, when dry, weighed 21 grams. The calculated for a mono salt is 16 grams, that for a disilver salt is 23.4 grams.

Dimethyl Derivative.—Ten grams of the disilver salt were suspended in ether and 15 grams of methyl iodide were added.

The mixture was heated in a closed tube at 98°–103° for 1.5 hours. The ether and excess of methyl iodide were evaporated and the residue extracted with alcohol. This gave a gummy extract which, when recrystallized from alcohol, yielded small prisms, melting at 254°–256°, with slight effervescence. The substance dissolved with difficulty in hot alcohol and was moderately soluble in hot water. It had a very bitter taste. A nitrogen determination (Kjeldahl), made after drying at 110°–120°, gave:

	Calculated for $C_7H_8O_4N_2$.	Found.
N	15.21	15.16

A *diethyl derivative* was prepared in a similar manner. It crystallized from alcohol, in which it is moderately soluble when cold, in the form of clusters of blunt prisms, melting at 162°–163°. In both of these reactions of the silver salt the chief product isolated was the free, unaltered acid which was obtained by extracting the residue with water. A nitrogen determination (Kjeldahl), in the case of the material melting at 162°–163°, showed that it was a diethyl derivative:

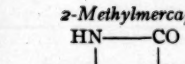
	Calculated for $C_9H_{12}O_4N_2$.	Found.
N	13.20	13.45

Ethoxymethylenemalonic ester and methyl pseudothiourea hydriodide were condensed, using 1 molecular proportion of potassium hydroxide. Under these conditions the free 2-methylmercapto-5-carbethoxy-6-oxypyrimidine did not separate but, instead, a poor yield of a basic hydriodide of the ester was obtained. A nitrogen determination (Kjeldahl) agreed with the calculated for a 2:1 salt:

	Calculated for $(C_9H_{10}O_4N_2S)_2HI$.	Found.
N	10.0	10.1

This salt forms needles from alcohol; when boiled with water, mercaptan was given off. It had no definite melting point.

2-Methylmercapto-5-carboxyl-6-oxypyrimidine,



above salt with potassium hydroxide and then precipitating with hydrochloric acid. It crystallized from hot water in well developed, colorless prisms, melting, to a clear oil, at 235°. Nitrogen determination (Kjeldahl):

	Calculated for $C_6H_6O_4N_2S$.	Found.
N	15.05	14.71

Our chief experiments were performed with the ethylmercapto derivatives, since they are more insoluble than the methyl compounds.

NEW HAVEN, CONN.,
January, 1907.

A POSSIBLE EXPLANATION OF THE INCREASE IN VISCOSITY WHICH RESULTS WHEN THE ALCOHOLS ARE MIXED WITH WATER; AND OF THE NEGATIVE VISCOSITY COEFFICIENTS OF CERTAIN SALTS WHEN DISSOLVED IN WATER.

[SEVENTH COMMUNICATION.]

BY HARRY C. JONES AND W. R. VEAZEY.

It is well known that when methyl or ethyl alcohol is mixed with water the viscosity of the mixture is much greater than that of either pure liquid. The following seems to us to be a possible explanation of this phenomenon:

It was shown some time ago by Jones and Murray[1] that when 2 associated liquids, such as formic acid and water, or acetic acid and water and, probably, such as alcohol and water, are mixed, each diminishes the association of the other. The result would be that in such a mixture there would be present

[1] THIS JOURNAL, 30, 205 (1903).

a *larger number of smaller molecules* than if the two liquids simply mixed without affecting each other's association.

This diminution in the association of the liquid molecules, increasing their number and diminishing their size, would increase the viscosity by increasing the total frictional surfaces of the molecules that would come in contact with one another—the smaller the molecules the larger the total surfaces of the molecules for a given mass of the liquid.

The above point can be illustrated by means of small shot and large shot. For a given mass, the smaller shot moving over one another would produce greater friction than the larger shot, due to the larger frictional surfaces that would come in contact. The same applies to the molecules of the mixed solvents.

The comparatively small association of the molecules of the mixed solvents, explains another phenomenon which has manifested itself in a number of the investigations[1] recently carried out in this laboratory. In those mixtures of solvents where the *viscosity is a maximum, the conductivity curve of many dissolved electrolytes shows a minimum.* As the conductivity curves, for the solutions of different concentrations of a given salt in different mixtures of 2 solvents, *approach the minimum, they approach one another.* This means that the molecular conductivities do not increase rapidly in these particular mixtures of the 2 solvents, with change in the dilution of the solution. This is exactly what would be expected if the molecules of the solvents in the mixture were only comparatively little associated. They would then have comparatively little dissociating power, and the conductivity in such a mixture of solvents would increase only slowly with increase in the dilution of the solution. The curves for molecular conductivity would, therefore, approach one another, as they approach the minimum.

It was observed in the course of our work that solutions of potassium sulphocyanate in water are *less viscous than pure*

[1] Jones and Lindsay: THIS JOURNAL, 28, 329 (1902). Jones and Carroll: *Ibid.*, 32, 521 (1904). Jones and Bingham: *Ibid.*, 34, 481 (1905). Jones and McMaster: *Ibid.*, 36, 325 (1906).

water. On looking up the literature that bears upon this problem, and especially the work of Wagner,[1] we find that a number of salts show this negative viscosity coefficient. They are potassium chloride, potassium nitrate, rubidium chloride and caesium chloride. Thallous nitrate also, apparently, shows the same phenomenon.

The explanation of this *negative viscosity coefficient* is comparatively simple, in the light of what has already been said in reference to viscosity.

The salts with the negative viscosity coefficient are, then, certain salts of potassium, rubidium and caesium. The case of thallous thallium will be considered a little later. If the *ions of the salt were very large*, relative to the molecules of the solvent, then the effect of the dissolved substance on the viscosity of the solvent would be to diminish it. This will be seen at once, if we think of a number of larger spheres mixed with a much larger number of smaller spheres. The frictional surfaces would be diminished and, consequently, the friction, when these spheres move over one another.

The question is whether there is any reason to suppose that the ions of potassium, rubidium and caesium are large. If we turn to the curve of atomic volumes[2] we find the answer. As is well known, potassium, rubidium and caesium occupy the maxima of the atomic volume curve, and these 3 elements have *much larger atomic volumes* than any other known elements.

The *qualitative* agreement of fact and theory are thus in accord, with the exception of the thallous salt. Since, however, we do not know at present the atomic volume of thallous thallium, this case will have to be left out of the discussion.

If we wish to test the above suggestion *quantitatively*, we have the means of doing so. Potassium has a much larger atomic volume (about 47) than any other element except rubidium and caesium. The atomic volume of rubidium is about 57, while the atomic volume of caesium is about 74. If we

[1] Z. physik. Chem., 3, 31 (1890).

[2] Lothar Meyer: Die Moderne Theorien der Chemie; Holleman: Inorganic Chemistry; Jones: Elements of Physical Chemistry.

compare the viscosities of the same salt of these 3 elements, say the chlorides, we should expect to find, in terms of our hypothesis, that the viscosity coefficient would be less for rubidium chloride than for potassium chloride, and less for caesium chloride than for rubidium chloride.

From the work of Wagner we can make the above comparison. The time of flow of pure water through the viscometer is taken as the unit of value for η. The values of η for normal solutions of potassium chloride, rubidium chloride and caesium chloride are:

	η.
Potassium chloride	0.9872
Rubidium "	0.9846
Caesium "	0.9775

It is worth noting that the difference between the values of η for caesium chloride and rubidium chloride is much greater than the difference between rubidium chloride and potassium chloride. This is in keeping with the relative atomic volumes of the 3 elements. The difference between the atomic volume of rubidium and caesium is much greater than the difference between the atomic volume of rubidium and potassium.

The question now arises whether, *e. g.*, all potassium salts show the negative viscosity coefficient. The answer is that they do not. The reason for this is obvious when we consider that the effect of a salt on the viscosity of a solvent is an additive function of both of the ions present in the solution. The anion, so far as we know, always tends to increase the viscosity of water, while certain cations, as those above considered, diminish the viscosity of water. The action of the salt, as a whole, upon the viscosity of water, is the algebraic sum of these effects, which may be either positive or negative.

Wagner[1] studied 6 salts of potassium in this connection, and found values of η less than unity only in the case of the chloride and nitrate. In the other 4 cases the action of the

[1] Z. physik. Chem., 5, 36, 37 (1890).

anion more than overcame the effect of the cation, and η was always greater than unity. *The chloride gave a negative value for* η. This would be expected, since *chlorine has itself a large atomic volume*; indeed, larger than that of any other elementary anion except bromine. This would, then, probably act in the same way as the potassium cation, giving a negative coefficient; or, if the coefficient due to chloride were positive, it would have a very small value.

For the same reason potassium nitrate shows a large negative viscosity coefficient.

If we extend the above conception to other cations with large atomic volumes, but with much smaller atomic volumes than the 3 alkalies, we shall find that it holds satisfactorily. Taking calcium, strontium and barium, which, of all cations, have the next larger atomic volumes, and comparing their chlorides with respect to the values of η, we have, for normal solutions:

	η.
Calcium chloride	1.1563
Strontium chloride	1.1411
Barium chloride	1.1228

These values are all positive, as we should expect them to be, but their order is exactly *the reverse of the atomic volumes*, just as would be expected.

Chlorides with cations of still smaller atomic volumes have values of η much larger than the above. This will be seen from the following table, where all the values of η refer to normal solutions. In the same table are given the approximate atomic volumes of the cations of the several chlorides:

	At. vol.	η.
Magnesium chloride	14	1.2015
Cupric "	8	1.2050
Manganous "	7	1.2089
Nickel "	7	1.2055
Cobalt "	7	1.2041

It is obvious that for the atomic volumes of the same order of magnitude, the values of η are of the same order of magni-

tude; and, in general, the larger the atomic volume the smaller the value of η, just as we should anticipate in terms of our hypothesis.

The small values of η for zinc, cadmium and mercury are probably due to the fact that the salts of these metals are only slightly dissociated.

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STUDIES IN CATALYSIS: THE REARRANGEMENT OF ACETYLHALOGENAMINOBENZENE DERIVATIVES INTO HALOGEN ACETANILIDE DERIVATIVES.

BY S. F. ACREE AND J. M. JOHNSON.

[The writers are indebted to the Carnegie Institution of Washington for aid in this work.]

Acetylchloraminobenzene[1] rearranges in the presence of hydrochloric acid into parachloracetanilide, but is stable under alkaline solutions. Blanksma[2] found that the velocity of the rearrangement increases as the square of the concentration of the acid increases, and that the reaction is one of the first order, or, apparently, monomolecular.

We have now found that the catalytic action of the acid is not due merely to the presence of the hydrogen ions, but that the acid unites with the acetylhalogenaminobenzene and forms another compound which rearranges into the halogen acetanilide,

(1) $CH_3CONClC_6H_5 + HCl \rightarrow CH_3CONHCl_2C_6H_5 \rightarrow CH_3CONHC_6H_4Cl + HCl.$

Acetylchloraminobenzene and hydrobromic acid give parabromacetanilide and the same product is obtained from acetylbromaminobenzene and hydrochloric acid. This is due to the fact that the bromine migrates much more rapidly than the chlorine to the benzene ring. Similarly, chlorine

[1] Slosson: Ber. d. chem. Ges., **28**, 3265. Armstrong: J. Chem. Soc., **77**, 1047. Chattaway and Orton: *Ibid.*, **75**, 1046; **77**, 134; **79**, 274; Ber. d. chem. Ges., **32**, 3573.
[2] Rec. Trav. Chim., **21**, 366; **22**, 290.

$$(2)\quad \begin{matrix} CH_3CONClC_6H_5 + HBr \\ CH_3CONBrC_6H_5 + HCl \\ CH_3CONHClBrC_6H_5 \end{matrix} \rightarrow CH_3CONHC_6H_4Br + HCl.$$

and bromine cause the change of acetylchloraminobenzene in a few seconds, in ligroin solution, into parachloracetanilide and parabromacetanilide, respectively. Quantitative measurements have shown the velocity constant for the change of acetylchloraminobenzene by hydrobromic acid to be about 1000 times as great as that for hydrochloric acid in the same concentration. Since solutions of sulphuric, acetic, hydrochloric and hydrobromic acids, having the same concentration of hydrogen ions, give different velocity constants, it is evident that the catalysis is not dependent directly upon the concentration of the hydrogen ions. The reaction between the hydrobromic acid and acetylchloraminobenzene is of the second order, whereas that produced by hydrochloric acid is of the first order, as demanded by equation (2).

The reaction is not dependent upon the rearrangement of an intermediate cathion formed from the weak base acetylhalogenaminobenzene and the hydrogen ions, as is probably the case in the hydrolysis of such weak bases as esters, amides, amidines and oximes. If such were the reaction, we should have, from Walker's equation,

$$(3)\quad CH_3CONClC_6H_5 + \overset{+}{H} \rightleftharpoons \overset{+}{CH_3CONHClC_6H_5};$$

or

$$(4)\quad C_{base} \times C_H = KC_{salt}.$$

The velocity of transformation of the substance would then be

$$(5)\quad \frac{dx}{dt} = K_{trans}\, C_{salt} = \frac{K_{trans}\ C_{base} \times C_H}{K},$$

or the velocity of rearrangement would be proportional to the concentration of the hydrogen ions, as we actually find in

the formation and saponification of esters, and the hydrolysis of acetamide.

But if the rearrangement is that of an intermediate undissociated salt, as was shown above, since the salt is greatly hydrolyzed and the small amount present is nearly completely dissociated, we have from the mass law:

$$(6)\quad CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows CH_3CONHCl_2C_6H_5,$$

or

$$(7)\quad C_{base} \times C_H \times C_{Cl} = KC_{salt} = C_{base} \times C_H^2 = C_{base} \times C_{Cl}^2.$$

The velocity of transformation of the substance would then be

$$(8)\quad \frac{dx}{dt} = K_{trans}\, C_{salt} = \frac{K_{trans}}{K} C_{base} \times C_H^2,$$

which is what is actually found experimentally. A further fact in support of this view is that the velocity of rearrangement becomes slower in those acetic acid solutions containing a greater percentage of water.

We have here a case, then, in which the velocity of a reaction is not proportional to the concentration of the catalyzing hydrogen ions, but to the square of that concentration. This fact at once leads to the conclusion that some reversible reaction may yet be found in which the equilibrium is changed by a change in the concentration of the catalyzer. The velocity of the reaction in one direction may be proportional to the m power of the concentration of the catalytic agent, whereas the velocity of the reverse reaction may be proportional to the n power of the concentration of the catalyzer, or

$$(9)\quad \frac{KC_{sub}}{K'C_{sub'}} = (C_{cat})^{\frac{m}{n}}.$$

Such a case seems to have been discovered recently by Baur and Voerman,[1] who showed that chromium nitride is a very energetic catalyzer of ammonia, in effecting its own formation from chromium and ammonia, but has no great influence

[1] Z. physik. Chem., 32, 467.

on the reverse reaction, or the formation of ammonia from hydrogen and nitrogen:

$$Cr + NH_3 \rightleftharpoons CrN + 3H.$$

The above theory of intermediate compounds in catalytic reactions is being investigated in several directions in this laboratory. We shall continue the study of the rearrangement of acylhalogenaminobenzene derivatives and other similar rearrangements.

JOHNS HOPKINS UNIVERSITY.

OBITUARY.

NICOLAI ALEXÁNDROWITSCH MENSCHUTKIN.

In the course of a few weeks Russia has lost her three most eminent chemists, Beilstein, Mendeléeff and Menschutkin.

Professor Menschutkin was born in St. Petersburg, October 12, 1842, and died in the same city February 5, 1907. He received the doctor degree from the University of St. Petersburg in 1866, and became professor of chemistry in the same institution in 1876. In 1902 he retired with the title of Professor Emeritus, but during the same year was appointed professor in the St. Petersburg Polytechnium. From 1868 to 1900 Menschutkin was editor of the "Journal of the Russian Physical-Chemical Society," and he wrote several text-books on analytical, organic and theoretical chemistry, and also a biographical dictionary of the professors of the University of St. Petersburg during the years 1869–94.

Menschutkin's fame as a chemist is based on his study of the velocity of certain organic reactions, especially those leading to the formation of esters and of ammonium derivatives. Besides investigating the influence of temperature, dilution, etc., on the velocity and conditions of equilibrium, he gave special attention to discovering the effect on ester formation, of difference in structure both of acids and alcohols, and was able to show how sharply and clearly the values measured by the physical chemist are correlated with the structural formulae assigned by the organic worker. Menschutkin was Vice-president of the Russian Physical-Chemical Society and a Foreign Member of the Chemical Society (London).

HENRI MOISSAN.

Professor Henri Moissan was born in Paris, September 28,

1852, and died in the same city, after an operation for appendicitis, February 20, 1907. Moissan spent his whole life in Paris; his doctorate was from the University of that city, and at the time of his death he was Professor of Chemistry at the Sorbonne and Director of the Laboratory of Mineralogical Chemistry. Moissan's fame as a chemist does not rest only on his great discoveries—the isolation of fluorine, the artificial production of the diamond and the invention and utilization of the electric furnace—his wonderful technique, his thoroughness, and the beauty, simplicity and modesty of the language in which his results were communicated to the world, had no small share in carrying instant conviction to any reader that the problem under consideration had been dealt with as fully and completely as contemporary skill and appliances permitted. His later work has been concerned largely with the preparation of binary compounds of the metals and non-metals; although less dramatic and, therefore, perhaps, less widely known than some of his earlier researches, such as that on artificial diamonds, it demanded as great, if not greater, skill and resource. It has led to the preparation by him, in the electric furnace, of large numbers of carbides, nitrides, silicides, borides, phosphides, etc.

Some of these substances have acquired considerable technical importance; all of them are of interest to the pure Chemist, but they appeal to a still wider circle. When their mode of formation and properties shall have become familiar to the Geologist, they can hardly fail to modify profoundly many of the present theories regarding the age and past history of the earth.

In contrast to his experiments with the electric furnace, his investigations on the possible existence of ammonium, NH_4, and other similar substances may be mentioned. Although he failed to obtain this complex, the researches demonstrated that his skill and fertility of resource, and the beauty and simplicity of the appliances which he designed were as great when working at the lowest, as at the highest attainable temperatures.

Moissan's books shared the same purity of diction and clarity of style which marked his papers. Besides those dealing with his own experiments, he edited the "Traité de Chimie Minérale," in 5 large volumes.

Moissan was the recipient of many marks of distinction from his fellow-chemists. He was a member of the Institute of France, Foreign Member of the London Chemical Society and Honorary Member of the American and German

Chemical Societies. He was the French member of the "International Committee on Atomic Weights," and at the end of last year was awarded the Nobel Prize.

HENDRIK WILLEM BAKHUIS-ROOZEBOOM.

Professor Bakhuis-Roozeboom was born at Alkmaar, North Holland, October 24, 1854, and died rather suddenly at Amsterdam, February 8, 1907. Roozeboom spent the whole of his active life at Leiden and Amsterdam. He was appointed Assistant in Chemistry in the former University in 1878, received the doctor degree from it in 1884, and was promoted to be "Lector" in 1890. Since 1896 he has been Professor of Inorganic and Physical Chemistry at the University of Amsterdam. Roozeboom is best known for his extensive researches into the nature of mixed crystals, of double salts and of racemic compounds, and for his work on the application of the phase rule to the results which he obtained from these investigations. He made numerous studies of heterogeneous equilibria from the phase rule standpoint, and published a volume on the subject in 1901. Roozeboom was an honorary member of the American Chemical Society.

REPORT.

Glyoxal.

The properties of the compound known as glyoxal are certainly not such as would be expected of a substance with the formula OCHCHO. Some text-books try to evade this difficulty by describing the body as a "hydrate" but, to say the least, this is unsatisfactory. C. Harries and Paul Temme[1] have made recently an important contribution to our knowledge of this interesting compound. Glyoxal exists in the following 4 forms: (1) Monomolecular glyoxal, OCHCHO, which is unstable and is described more fully below. (2) A trimolecular modification, $(C_2H_2O_2)_3$, which may possibly have the formula OCHCH(OH)COCH(OH)COCHO. It is a colorless, pulverulent solid, readily soluble in water and forms no characteristic derivatives, *i. e.*, reagents give with it only derivatives of 1. (3) Paraglyoxal, $(C_2H_2O_2)_x$, a white powder, insoluble in water. (4) The ordinary form of glyoxal, termed polyglyoxal, $(C_2H_2O_2)_n$. This was discovered 50 years ago by Debus, and is the substance described in text-books and in

[1] Ber. d. chem. Ges., 40, 165 (1907).

catalogues of chemicals. Compound No. 2 reduces Fehling's solution, but Nos. 3 and 4 do not.

Monomolecular glyoxal is prepared by distilling a mixture of technical "glyoxal" (4) with phosphorus pentoxide, and condensing the distillate by means of solid carbon dioxide and ether. Care must be taken to avoid the presence of moisture in the apparatus. The compound crystallizes in yellow prisms or spangles, becomes opaque at 10°, melts at 15° and boils at 51° (776 mm.), or 50° (742 mm.). The vapor is intensely emerald-green and condenses to a liquid which is at first green; as this is cooled it becomes yellow and, at very low temperatures, colorless. The vapor has an odor like that of formic aldehyde, but as inhalation continues the smell becomes sweet and not disagreeable. It burns with a violet flame and forms with air a mixture which explodes violently on the application of a flame. Glyoxal changes spontaneously into paraglyoxal (3) in a few hours. Its vapor density and refractive power agree with the simple formula. Its reaction with water is very interesting. The addition of a small quantity of water to glyoxal causes immediate polymerization to paraglyoxal (3), whereas, if glyoxal be added to a large quantity of water, it dissolves readily with a hissing noise and the solution, which becomes decidedly acid, contains monomolecular glyoxal, as is shown by cryoscopic measurements. If this solution is boiled, the glyoxal volatilizes with the steam. It reduces ammoniacal silver solution, but not Fehling's solution, in this latter respect resembling the poly- and para-modifications. It is chiefly on this fact that the formula for trimolecular glyoxal is based.

Trimolecular glyoxal is readily prepared by the action of water on cinnamic aldehyde ozonide.[1] The oily product, consisting of benzoic acid and, apparently, of benzoic aldehyde, is removed, and the aqueous solution concentrated at 30°–40°, *in vacuo*. If the temperature is allowed to rise above 40°, the substance finally isolated resembles commercial glyoxal (4) more or less closely, and has, to a varying degree, the power of reducing Fehling's solution.

Attention may be called to the fact that in being strongly colored, monomolecular glyoxal resembles the α-diketones, such as diacetyl. Moreover, of the compounds containing only carbon, hydrogen and oxygen, glyoxal is probably the simplest one to possess a color. It is of interest to remember, in this connection, that oxalic acid shows not the slightest sign of color, although it also contains the grouping OCCO,

[1] Cf. THIS JOURNAL, 38, 463 (1906).

but, of course, with 2 hydroxyls instead of 2 hydrogen atoms. The study of these 2 substances by Baly's method[1] could hardly fail to yield results of considerable interest.

J. BISHOP TINGLE.

REVIEWS.

THE HISTORICAL DEVELOPMENT OF CHEMISTRY. By WILHELM OSTWALD. [Reprinted from the School of Mines Quarterly, Vol. XXVII, Nos. 2–4]. New York. pp. 84.

As stated by the author, this pamphlet is made up of six lectures delivered in the Department of Chemistry of Columbia University in January and February, 1906. The lectures were reported stenographically. Ostwald is always interesting and always thoughtful, perhaps interesting because thoughtful. He is, as he himself says, a philosopher. He is looking for the hidden causes of phenomena, and trying to distinguish the essential from the non-essential. He has a mortal terror of hypotheses. He clearly recognizes the danger connected with their use, but apparently does not recognize their value, or at all events he minimizes it.

In discussing the difference between mixtures, solutions and chemical individuals he says: "Mixtures are therefore substances which can be identified as *heterogeneous* by physical means. Solutions are substances which are *homogeneous*. But now what is the difference between a solution and a chemical individual?" * * * * "To describe this difference in scientific terms I shall have to go back to a most important work of Josiah Willard Gibbs, late professor of mathematical physics at Yale University, and I do not hesitate a moment to speak of him as by far the greatest scientist America has as yet produced." He then gives a brief exposition of the phase rule and proceeds thus: "When, therefore, we wish to know if a homogeneous thing is a solution, a substance, or a chemical individual, we have only to change it to another phase; if in this changing into another phase the change is connected with no change in the remaining portion, then it is a chemical individual. Otherwise it is a solution."

His definition of an element is this: "*An element is a substance or chemical individual which never becomes a solution or mixture.*"

[1] THIS JOURNAL, 36, 213 (1906).

The discussion of the atomic hypothesis and the law of combining weights furnishes a good illustration of the author's effort to eliminate the hypothetical. That we *can* deal with the laws of definite and multiple proportions and with combining weights without mentioning or even assuming the existence of atoms is well known, but whether anything is gained by doing so is questionable, to say the least. The general opinion among thinking chemists is that the atomic hypothesis does more good than harm.

In treating of the molecular hypothesis the author admits that by its aid "the whole system of organic chemistry can be made much more simple and much more logically related than otherwise." He goes on to say: "Then after this served as an introduction, the molecular hypothesis in chemistry went on rather quickly and emphatically. You will find certain definitions in every text-book—I have not been able to trace the first inventor, but it would be interesting to do so—that atoms are the smallest possible parts of matter which cannot be divided any more, or which, by division, would yield other kinds of matter, and molecules are the smallest particles existing in gases or capable of existing in gases. Now it is the queerest thing that no body ever tried to carry out any experiments to show the truth or to show the scientific meaning of these definitions. Nobody tried to find the smallest particle of a gas and determine its quantity."

The writer of this notice, in his blindness, has hitherto supposed that both the atomic hypothesis and the molecular hypothesis are in harmony with a very large number of facts that have been established experimentally. If this be true, then both hypotheses can be said to have a broad experimental basis. If it were possible to isolate an atom and a molecule and to show by worldly means that they are what we assume them to be, we should all rejoice, but the prospects are not alluring. Meanwhile, must we wait until evidence of this kind shall have been presented?

Of course, organic chemistry comes in for a fling. The author thinks that it is *possible* to deal with all the facts of this branch of chemistry without the assumption of atoms and linkage of atoms. He adds: "*I* think it is possible, but it would be an enormous task, and would take a young man who has still his entire life potential to exert, for this will be a very large and difficult piece of work." I. R.

TOXICOLOGY, THE NATURE, EFFECTS AND DETECTION OF POISONS WITH THE DIAGNOSIS AND TREATMENT OF POISONING. By CASSIUS M. RILEY, M.D., Professor of Chemistry and Toxicology in Barnes University, and Dean of the Barnes College of Pharmacy, etc. Third Edition Revised and Enlarged. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 215. Price, $1.50 net.

The author states that he has sought to present to the busy practitioner a convenient work of reference which contains in concise form the present-day knowledge on this subject. The book differs in no essential way from many others which have appeared. Such statements as the following (p. 8) could have been omitted with profit: "——the more unstable alkaloids and poisons are oxidized in their passage through the lungs." And again on the same page, "Phagocytosis is still disputed by some investigators, but the weight of opinion seems to favor the theory . . . ." etc., etc. Each poison is considered under the following heads: Properties of the Substance, Symptoms, Diagnosis, Fatal Dose, Fatal Period, Treatment, Post Mortem Appearances, Detection. All elaborate chemical methods are omitted. Thus, even Marsh's test for arsenic is not given. The style is clear and concise and the book answers the purpose of the author very well, that is, it will prove a handy book for physicians. A. S. L.

AUSFÜHRLICHES LEHRBUCH DER PHARMAZEUTISCHEN CHEMIE. Bearbeitet von DR. ERNST SCHMIDT, Geh. Regierungsrath, O. Professor der pharmazeutischen Chemie and Direktor des pharmazeutisch-chemischen Instituts der Universität Marburg. Erster Band. Anorganische Chemie. Erste Abtheilung. Metalloide. Fünfte vermehrte Auflage, mit zahlreichen Abbildungen und einer farbigen Spektraltafel. Braunschweig: Fr. Vieweg u. Sohn. 1906. pp. 523. Price, M. 10.

This first instalment of Vol. I. of Professor Schmidt's well-known handbook deals with general chemistry, 114 pp., and with the non-metals, 404 pp.

In the chapter on general chemistry the author makes brief mention and explanation of electrolytic dissociation, mass action and other modern views. The remainder of the volume is purely descriptive. All laboratory and technical methods of preparing elements and compounds are very fully described; for example, 2 pages are given to the preparation of basic bismuth nitrate and to tests of its purity. There are detailed instructions in analytical methods; for example, of 38 pages given to the discussion of water, 23 are filled with details of water analysis; of 12 pages given to phosphorus, 5 describe its detection. We see, then, that this is not a text-book of inorganic chemistry in the ordinary sense, but a combination of one with analytical and preparative treatises.

The system of quarantining chemical theory in an initial

chapter—apparently lest the purely descriptive matter should "catch" some germ of theory—is a method very common in German text-books of the period preceding Ostwald, and survives in later editions of such books. Generally, the system is open to severe criticism, but in the present case there is much to be said in favor of it. No one would use Professor Schmidt's book who had not previously studied chemistry with the help of a smaller work, and the practical use of this volume is as a reference and handbook for pharmacists; for this purpose the arrangement is excellent.

The revision seems thorough; but few omissions are noticeable; no mention is made of the solidification of oxygen, nor of the hydrides NaH and KH, though the alloys of these metals with hydrogen, K_4H_2 and Na_4H_2, approximately, are referred to.

In brief, the first instalment of Professor Schmidt's book indicates that the work, as a whole, will retain its high position as a handbook almost indispensable to pharmacists.

E. R.

THE CHEMISTRY AND PHYSICS OF DYEING. By W. P. DREAPER, F.I.C., F.C.S. Illustrated by Curves and Numerous Tabulated Results. Philadelphia: P. Blakiston's Sons & Co. 1906. Price, $3.00 net.

Although many investigators have published independent articles in regard to the purely scientific relations existing between textile fibers and coloring matters, the above work is the first, in the English language at least, which brings together in one volume a general record of the important work that has been done along this line.

The modern textile colorist is so absorbed with the commercial success of his work, that he overlooks the fact that a more thorough knowledge of the physical and chemical relations existing between fiber and coloring matter would, ultimately, lead to the improvement of the processes he is using, as well as to the introduction of great economies. Many of the more progressive textile colorists undoubtedly realize the desirability of such a knowledge, but the demands upon their time are such that it is impossible for them to go through all the journals and extract from this and that one the facts which have been discovered and the theories which have been formulated by the many investigators. To such, this volume will prove of great value, for the author has succeeded in bringing together the essence of the work of many workers, and with the interjection of certain views of his own, has presented an interesting and valuable résumé of the work

that has been done by the scientist toward the elucidation of the exact nature of the process of textile coloring.

The historical introduction goes back to a period 1500 B. C., when wool dyed with the celebrated Tyrian Purple, sold for a price corresponding to $150 per pound, and includes a bibliography of the early publications in regard to dyeing. In this connection it might be noted that the extensive works of Edward Bancroft, M.D., one of the pioneer investigators, which were published between 1769 and 1814 were overlooked, although reference is made later in the book to Bancroft's classification of dyestuffs into substantive and adjective coloring matters, which for many years was about the only accepted classification.

The chapter on the properties of the fibers and their reactions enumerates the important facts which have been discovered concerning the chemical nature of the textile fibers and their action in contact with reagents. The author's statement to the effect that the complex chemical nature of the textile fibers has rendered the knowledge in regard to them very limited and unsatisfactory is, unfortunately, too true, but as the study of colloid substances is continued and new facts are discovered in regard to their nature, it is hoped that much can be done toward clearing up many relations existing between fibers and coloring matters which are but little understood at the present time. The author has certainly taken the proper view of the matter, for it is evident that he thoroughly believes that the keynote to the interpretation of the facts already discovered, and the hopes of future development, depend largely upon our present knowledge of solution and the properties of colloids and the advancement that may be made through their study.

The 3 long chapters which treat, in the main, upon solution and colloids, are well worth the careful study of the textile chemist and colorist, for one cannot help being introduced to entirely new lines of thought and reasoning when they are taught to apply the principles of the modern science of physical chemistry to their study of the phenomena of textile coloring.

Whether or not the dyeing process is, in the majority of cases, of a physical or a chemical nature, is still an open question, but during recent years chemists have come more and more to believe that chemical action is involved in the application of many dyestuffs, particularly the two classes known as the acid and basic coloring matters. In the 2 chapters entitled, "Evidence of Chemical Action in Dyeing," the author

presents, in a systematical manner, all the evidence he has been able to collect from the journals and the writings of investigators, as far back as Dufay in 1737, but, as he says in the closing paragraph, "Until the time comes when we are able to explain the actions which take place when colloids react in the presence of solvents and definitely assign to these phenomena their true nature, it will be difficult to establish a strictly chemical basis for the reactions which take place in dyeing."

Another chapter deals with the influence of light during dyeing operations and upon dyed fabrics, subjects in regard to which but little exact information is obtainable, but the author goes into considerable detail with the material at hand.

The closing chapter of the book, entitled "Methods of Research," though short, is very expressive of the general spirit of the whole book, namely, a plea for more thorough, exact and extensive investigation of the fundamental facts and theories of the various textile coloring operations. The author should be given credit for having been willing and able to break away from the purely commercial aspect of the subject, and for having presented a work which must necessarily set many readers to thinking along new channels and prove an element in the uplifting of textile coloring as a more exact science.

L. A. OLNEY.

ESSENTIALS OF CRYSTALLOGRAPHY. By EDWARD HENRY KRAUS, Ph.D., Junior Professor of Mineralogy, University of Michigan. 8vo, pp. xl + 162 and 427 figures. Ann Arbor, Mich.: Geo. Wahr. 1906. Price, $1.60.

This little book, prepared by Professor Kraus, will doubtless prove serviceable to instructors in crystallography, because of its many illustrations and tables of crystal forms. It may likewise prove serviceable to chemists familiar with the older forms of crystallographic nomenclature, since these are here brought into association with the new terms based on 32 classes. The free use of varied standard text-books recognized in the preface is evident throughout the book. Without wishing to criticize severely, the reviewer questions the advisability of retaining the old method of discussing hemihedrism and hemimorphism by the assumption of the suppression of given faces. Each suppression is contrary to the methods of formation of the so-called partial forms, and the advantages arising therefrom are not equal to the misconceptions which the student almost always acquires.

E. B. M.

NOTES ON MILITARY EXPLOSIVES. By ERASMUS M. WEAVER, Major, Artillery Corps, U. S. Army; General Staff Detail. Late Instructor in charge of the Department of Artillery Chemistry and Explosives, Artillery School, Fort Monroe, Va., and Artillery Inspector Atlantic Division. First Edition. New York: John Wiley & Sons. 1906. pp. 311. Price, $3.00 net.

The author says: "These notes were collected with a view to lecturing on the subject of Modern Military Explosives to the student officers at the Artillery School, Fort Monroe, Va. It was desired to give the officers a general knowledge of the modern explosives, including the composition and manufacture of the important military explosives; the general chemical and physical principles involved in explosive phenomena; the principles governing the storage, handling and uses of explosives in demolitions and disruptive work."

The book seems, on the whole, well adapted to the purpose. The author, from a military point of view, divides explosives into 3 classes: Progressive or propelling; detonating or disruptive; and exploders. The first class includes charcoal powders and nitrocellulose powders; the second includes guncotton, nitroglycerin, dynamite, explosive gelatin, and derivatives of picric acid; the third treats of fulminates.

The chapters on the storage and handling of explosives and their use for demolitions are excellent, as would be expected from an author who knows the subject both practically and theoretically, and has also had the teachers' experience.

The least satisfactory part of the volume is the introductory chapter on the principles of chemistry, in 47 pages. This chapter is included because "some of the officers have little or no knowledge of chemistry." This would, doubtless, be a bar to an intelligent study of explosives, but that the deficiency could be made good by studying the extremely condensed material given here, even with laboratory work, seems doubtful. E. R.

BEET-SUGAR MANUFACTURE. By H. CLASSEN, Ph.D., translated from the Second German Edition by Wm. T. Hall and Geo. Wm. Rolfe, Instructors in the Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1906. pp. xiv + 280. Price, $3.00 net.

This book gives a condensed review of the principal processes involved in the manufacture of beet sugar. It brings the technique of the processes up to the year 1903. The rapid growth of the beet sugar industry in this country justifies the publication of elementary works of the character of the present one. The translators have done the original into good English, and placed the work at the service of the non-

German reading expert. There is nothing new or novel in the contents of the book. It is interesting to note that the author considers lime and carbon dioxide as the best and cheapest agents in the purification of the diffusion juice. He states that the use of sulphurous acid, aluminum sulphate and the electric current has not been proved profitable or advisable. It is, doubtless, true that the same principle holds with cane juice, and the use of such injurious substances as sulphurous acid will probably soon cease, especially when the resulting molasses is intended for human food. A most interesting chapter, from a technical point of view, is that relating to the treatment of sludge or scums. This matter is presented in admirable form. The chapter on sugar is given in detail and will be found especially valuable to beginners. A useful chapter is also that devoted to molasses and its utilization, particularly its consumption as a cattle food. The final chapter, on the utilization of the waste products, is also interesting. The appendix contains formulae, tables of data, etc.

The work will be found useful to those engaged in the cane sugar industry, as well as to those who manufacture sugar from the beet.

H. W. WILEY.